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MOLECULAR PHYSICS OF EQUILIBRIUM GASES

A Handbook for Engineers

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A Handbook for Engineers

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PREFACE

Molecular physics is deemed here to include the physics of fundamental particles such as atoms and electrons as well as of more complex molecular structures formed from these basic building units. The subject is one of wide utility and is rich in beauty. Its usefulness appears in every field of engineering and technology concerned with matter, that is, in every physical area of human endeavor. The conquest of space, the conservation of earth resources, and the promotion of health and ecology are but a few examples of present social concerns that ultimately rest on an understanding of molecular science. To be sure, the direct application may often be more than one link in the chain removed from the basic science, but the linkage is nevertheless always there whenever one deals with matter in any form. The bulk properties of matter which the engineer uses to solve practical problems are all appropriate averages of basic atomic and molecular properties. To deny the importance of this linkage is to deny the technology the roots from which it grows. Obviously, any society that depends on its technology for leadership in the world community must promote a healthy competence in such fundamental science if it is to maintain this leadership.

The beauty of molecular physics is less easy to define than its usefulness, but it is unmistakable. To the scientist the logical framework of the subject is impressive, to the artist and architect the variety of structure and form evoke admiration, and to the mathematician the elegance of the symmetry relations involved holds exceptional appeal. To the mystic, the science of molecules is a pattern of creation in the physical universe suggesting similar patterns of creation on other planes of reality. Moreover, the atomic and molecular sciences are now reasonably mature and permit one to classify extensively and make broad generalizations. Philosopher Hans Reichenbach has said that generalization is the very essence of knowledge, so molecular theory partakes of this quality of all true knowledge.

The present book is concerned only with the evaluation of equilibrium thermodynamic properties of gases and some applications to engineering problems. This subject has been developed traditionally by the physical chemist, but the basic theory and experimental data are now so complete that the subject logically should be taken up by the engineer to work out the detailed approximations needed for his applications. This book attempts to give the engineer a background for this task.

To solve gasdynamic problems in general, the engineer also needs a well-developed science of transport processes, of chemical rate processes, and of radiation. The first of these is already a standard engineering subject and is well treated by recent engineering texts such as "Mathematical Theory of Transport Processes in Gases" by J. H. Ferziger and H. G. Kaper (North Holland-American Elsevier Publishing Co., 1972) and "Introduction to Physical Gasdynamics" by W. G. Vincenti and C. H. Kruger (John Wiley & Sons, Inc., 1965).

The other two topics (chemical rate processes and radiation) are reasonably well developed from a physicist's or physical chemist's point of view, but are yet in their infancy so far as engineering applications are concerned. For example, the theoretical physicist and chemist know the form of the matrix elements for perturbation-induced transitions between states, but the engineer or applied scientist has been unable to calculate simple rate coefficients, or even the perturbation potentials between colliding particles that determine the rate coefficients, or simple f-numbers and radiation band strengths. This occurs because the wave functions for multi-electron atoms and molecules cannot be calculated with sufficient precision; thus the engineer is forced to rely on meager and sometimes uncertain experimental data, and shrewd extrapolations of such data, to obtain the reaction rates and band strengths needed. However, this situation is rapidly changing. Fast, powerful digital computers are emerging which will soon allow us to calculate sufficiently accurate wave functions for many purposes. The time is approaching when the experimentalist will concentrate on highly accurate, unambiguous measurements at a few select and carefully controlled conditions, which can be used to validate the theoretical model programmed on the computer, whereas in the past the experimenters have attempted to make measurements over as wide a range of conditions as possible to provide the engineering data needed. Computer solutions will still make use of approximations because the speed and memory size needed to do so-called "exact" solutions are still about two orders of magnitude beyond present capability despite the tremendous recent advances in computer technology. Thus, the experimenter will retain a key role in validating these programs, even though the computer will be used to do extrapolations to conditions of interest. Such computer usage will open up the fields of reaction chemistry and radiation to full and practical quantitative applications by the engineers. Although this book does not include these subjects, the present material on equilibrium states and properties of gases is necessary background for the engineer who will pursue and use nonequilibrium properties of gases.

Several additional books have been aimed at a similar audience of aerodynamicists and engineers working on systems involving real gas behavior. Among these are "The Dynamics of Real Gases" by J. F. Clarke and M. McChesney (Butterworths, 1964), "Atomic Theory of Gas Dynamics" by J. W. Bond, K. M. Watson, and J. A. Welch (Addison-Wesley, 1965), "Physics of Shock Waves and High Temperature Hydrodynamic Phenomena" by Y. B. Zel'dovich and Y. P. Raiser (translated and edited by W. D. Hayes and R. F. Probstein, Academic Press, 1967), as well as the books by Vincenti and Kruger and by Ferziger and Kaper which were cited above in connection with the transport properties of gases. In addition, "The Molecular Theory of Gases and Liquids" by J. O. Hirschfelder, C. F. Curtiss and R. B. Bird (John Wiley and Sons, 1954) has been widely used by engineers and basic scientists alike. The present book puts less emphasis on gasdynamics than the above texts, but treats the molecular physics and structure aspects of the problem in greater detail.

Atomic and molecular physics have now become a part of graduate engineering curriculum, in recognition of the fact that these subjects are included in the background a research engineer needs to attack his problems. In the normal course of evolution, the basic scientist formulates and establishes the fundamental concepts in a field of science, and then tutors the engineer in the application of these concepts. As the field matures and becomes reasonably self-consistent, the basic scientist turns to newer areas of science, and the engineering field gradually absorbs the established science into its own curriculum.

In any case, the engineer is best served by ultimately assuming responibility for his own development of the intellectual tools of his profession. Approaches particularly suited to the engineer's needs are often not well suited to the basic scientist's viewpoints and vice versa. For example, knowledge of atomic and molecular properties is an end in itself to the physicist, but to the engineer these properties may be just a collection of coefficients needed to predict the behavior of a total system. It is the mark of a good scientist to refine his theoretical models, and their experimental confirmation, until they are as detailed and precise as possible. It is the mark of a good engineer to use models just sufficiently detailed to achieve the accuracy required and no more. Thus, it behooves the engineer to approach atomic and molecular processes from this point of view.

In the above spirit, this book deliberately emphasizes analytic models of the atomic processes, often to the point of considerable oversimplification, which convey at a glance the dominant functional behavior involved. To paraphrase an old Chinese proverb, "One analytic model is worth 10,000 hours on the computer." Such models help the engineer think effectively about the total system, and they yield the natural dimensionless parameters with which to analyze the problem. The engineer often finds that he can make comparisons with experiment and modify the constants that appear in very simple models to achieve the accuracy he needs.

Whether simple or not, a mathematical relation cannot really be used wisely until its derivation has been followed in detail so that its limitations are appreciated. The problem here is that the research engineer is faced with such a swelling torrent of published results to digest in a wide variety of fields that he cannot possibly take time to fill in all the derivations, which are necessarily abbreviated or deleted in the specialist's literature, even though he may be perfectly capable of doing so. Thus, one of the purposes of this book is to present derivations in considerable detail so that the reader can follow them quickly, recognize the potentials and limitations inherent in the model, and then profitably use his time elsewhere. Although such derivations are given only for simplified models, they will often be sufficient to provide a good intuitive grasp of the more detailed models encountered in the literature.

The reader is presumed to be acquainted with kinetic theory, thermodynamics, and elementary statistical mechanics and quantum mechanics, and to have a working knowledge of complex variables and the usual differential and integral calculus, all of which is standard for upper division or graduate engineers today. Concise derivations of some fundamental relations in statistical and quantum mechanics are included (although these are not needed by readers with the background specified above) because it is felt that engineers whose background in these subjects has lain unused for a time can then use the book more effectively. In addition, these short derivations are useful mnemonic aids that organize the essential relations, even for the advanced student, and their presentation provides the opportunity to call attention to viewpoints particularly adapted to an engineering approach.

Consistent with the purpose of making the derivations easy to follow, there has been an attempt to avoid complicated notation, involving a plethora of superscripts and subscripts. For example, vector notation is used when it seems to contribute to the understanding of the relations discussed, but the vector symbols are merely dropped whenever the issue concerns just the magnitudes of the vectors, rather than resorting to the rather cumbersome absolute magnitude signs about the vector symbols. Such notations do help retain generality, of course, but they are inimical to rapid comprehension and effective thinking. On the other hand, notation and dimensions are chosen appropriate to the topic under discussion, rather than for consistency. The specialist can afford the luxury of treating problems in a single, consistent set of units, but the engineer has no choice but to learn to be at ease with any system of units if he is to draw on the specialized knowledge in a variety of fields and bring it to bear on his problems. Equations are transformed to dimensionless form, where appropriate, because the essential relations can usually be more readily recognized and brought into focus in this form.

I have often been privileged to function as an interface between the basic sciences and the engineering approach to research problems. I have found this to be a stimulating function, for it forces one to attempt to formulate the essence of physical phenomena in as simple and direct a way as possible, yet maintaining an awareness of the limitations in accuracy of the models used. The material in this book is chosen primarily for its tutorial or heuristic value, so it is in no sense a complete exposition of the myriad of approximate models of atomic and molecular properties found useful for engineering needs. The primary purpose is to provide the engineer with those physical concepts about atoms and molecules which will enable him to digest research literature more efficiently. Hopefully, he will then be in a position to bring himself up to date with current archive literature in those areas pertaining to his particular needs.

The material contained in the book was first presented in a series of lectures to graduate students in Fluid Mechanics and in Aerodynamics at Massachusetts Institute of Technology (1965-66) as a course entitled "Atomic and Molecular Kinetic Processes." I am indebted to Professors R. F. Probstein, J. A. Fay, and J. C. Keck for the opportunity of preparing and delivering those lectures. In subsequent years, the material has been expanded and updated as a set of notes for training seminars attended by research engineers of the Fluid Mechanics Branch, the Magnetoplasmadynamics Branch, and the Physical Gasdynamics and Lasers Branch at Ames Research Center of NASA. Recently, the notes were again revised for use as lecture material for a graduate course in Aeronautics and Astronautics Engineering at Stanford University (1973-74) entitled "Molecular Physics of Gasdynamic Flow." I am indebted to Professor Daniel Bershader for this opportunity to update the notes. The students at M.I.T. and Stanford, research engineers at NASA, and other colleagues in the aerospace industry have all provided valuable suggestions about their needs in basic physics of gases, and this book attempts to address some of those needs.

The labor of preparing this book would increase enormously if I were to attempt to give full credit to all the sources and people who contributed in one way or another. My greatest debt is to Dr. Frederick Otto Koenig, recently Emeritus Professor of chemistry at Stanford University, for the superb lectures on statistical and quantum mechanics he gave many years ago. I also want to credit B. E. Cunningham, NASA, for his help in preparing some of the material in chapter 10. Valuable criticism and editing was provided by my students and by my colleagues at Ames Research Center - Drs. John R. Viegas, David M. Cooper, Robert L. McKenzie, and Kenneth K. Yoshikawa. Undoubtedly, some of my errors remain; I hope these are minor in number and degree.

The references cited merely represent a few that have become classics or that I have found helpful; they do not in any way constitute a full bibliography. However, the material treated is now reasonably stabilized and self-consistent, so the brevity of the bibliography should not seriously detract from the tutorial purpose of the book. The aim is not so much to make the material complete, as this would require many additional volumes, but to present an engineering approach to a subject that has formerly been considered to be entirely in the domain of basic physics and chemistry and to demonstrate some of the advantages of such an approach.

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CHAPTER 1 - THERMODYNAMICS AND STATISTICAL MECHANICS

1.1 SUMMARY

The basic thermodynamic properties of gases are reviewed and the relations between them are derived from the first and second laws. The elements of statistical mechanics are then formulated and the partition function is derived. The classical form of the partition function is used to obtain the Maxwell-Boltzmann distribution of kinetic energies in the gas phase and the equipartition of energy theorem is given in its most general form. The thermodynamic properties are all derived as functions of the partition function. Quantum statistics are reviewed briefly and the differences between the Boltzmann distribution function for classical particles and the Fermi-Dirac and Bose-Einstein distributions for quantum particles are discussed.

1.2 INTRODUCTION

Properties of atoms and molecules are normally defined to be intrinsic for the gaseous state, that is, they are assumed to be properties only of the particles themselves and independent of the state of the gas. Among such properties are the quantum numbers of the particle, collision cross sections for scattering or internal energy excitation, dipole moment, etc. Strictly speaking, this assumption is valid only for the dilute gases; if the density of the gas becomes large, the atomic and molecular properties are all affected by perturbations from neighboring particles. For example, the perturbed quantum state can be described as a linear combination of unperturbed quantum states, and all other properties of the particle are affected accordingly. Nevertheless, a very useful model of the gaseous state is one in which the bulk properties of the gas are taken to be intrinsic molecular properties averaged over the distribution of particles in the various unperturbed quantum states. The effects of high density and pressure are then analyzed as small perturbations to this model.

The engineer is, of course, ultimately interested in the bulk properties of the gas, which may be classified as either intensive or extensive. An intensive property is a function of position and does not depend on the specific amount of gas considered, whereas an extensive property represents an average per unit quantity of gas which is to be multiplied by the total quantity of gas to obtain the total value of the property for the system. The three most commonly used intensive properties are temperature, T; pressure, p; and density, ρ.

For the extensive properties, the capital letter notation is traditionally taken to represent the average value per mol of gas (i.e., per Avagadro number - 6.025×10^{23} - of molecules) whereas lower case letters are used to represent the value per unit mass. For example, the extensive properties per mol of interest here are

M	molecular weight per mol
V or $\frac{M}{\rho}$	volume per mol
E	energy per mole
H or $E+pV$	enthalpy per mol
S	entropy per mol
C_v or $\left(\frac{\partial E}{\partial T}\right)_V$	specific heat per mol at constant volume or density
C_p or $\left(\frac{\partial H}{\partial T}\right)_p$	specific heat per mol at constant pressure
F or $E-TS$	free energy per mol or Helmholtz free energy
G or $H-TS$	free enthalpy per mol or Gibbs free energy

(Note that A is sometimes used for the Helmholtz free energy, and F for the Gibbs free energy.)

Fluid dynamicists are usually interested in average properties per unit mass rather than per mol because, in these units, the thermodynamic quantities relate most directly to the flow velocity. For example, the sum of the enthalpy per unit mass and the kinetic energy per unit mass is a constant of steady adiabatic inviscid fluid flow. The most commonly used bulk properties per unit mass are:

$e = E/M$	energy per unit mass
$h = H/M$	enthalpy per unit mass
$c_v = C_v/M$	constant volume specific heat per unit mass
$c_p = C_p/M$	constant pressure specific heat per unit mass

1.3 REVIEW OF THERMODYNAMIC RELATIONS

A brief review of some of the relations that exist between the thermodynamic quantities will be helpful (refs. 1-3). These may be derived from the first and second laws of thermodynamics, stated here in differential form.

First Law of Thermodynamics (Conservation of Energy)

Every system has an energy E such that, for any change in which the total number of particles is conserved,

$$dE = dq + dw \tag{1.1}$$

where dq is defined as the heat *absorbed* by the system and dw as the work done *on* the system. The latter is a purely mechanical quantity, force times distance, which for a gas phase system is normally just

$$dw = -p\ dV \tag{1.2}$$

Note that dw vanishes for a constant volume process.

Second Law of Thermodynamics (Law of Entropy)

Every system has an entropy S and an absolute temperature T such that, for any change in which the total quantity of matter is conserved,

$$dq \leq T\ dS \tag{1.3}$$

The equality sign gives the lower bound on the change of entropy which obtains when the process is completely reversible.

Consider the heat flux from a system at temperature T_2 to a system at temperature T_1 where $T_2 > T_1 > 0$. The total change in entropy of the two systems is always positive:

$$dS = dS_1 + dS_2 \geq dq \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \geq 0 \tag{1.4}$$

The flow of heat from a hotter to a cooler system is a spontaneous, irreversible process, and the inequality signs in equations (1.3) and (1.4) hold for such cases. However, in principle, an experiment can be imagined in which the temperature difference is so minute that the process is almost reversible. The equality sign in equation (1.4) then gives the lower bound on the entropy increase. At equilibrium, the processes that occur in a system become completely reversible by definition, temperature differences must be zero, and the entropy becomes a maximum subject to the constraints imposed on the system.

The above result for two systems can be generalized to include an arbitrary number of systems, indeed the entire universe, and for processes other than heat flux, such as mass flux, pressure change, energy change, work, etc. The total change in entropy for any real process is always greater than zero.

For convenience in the derivations to follow, a closed system is defined as one that allows neither mass addition nor subtraction, but does allow energy or heat flux to and from the system. Conversely, an open system (a concept discussed in the chapter on Chemical Equilibrium) allows mass addition or subtraction also. For the present, we consider relations between the properties of a closed gas phase system. For such a system, it follows from equations (1.1), (1.2), and (1.3) that

$$dE + p\,dV - T\,dS \le 0 \qquad (1.5)$$

The equality holds if the processes are all reversible, that is, if changes are made so slowly that the system always maintains equilibrium. In reality, a system must be driven out of equilibrium to make a process occur and change the state of the system starting from equilibrium. However, in principle, the amount of nonequilibrium can be kept so small that the equality is an extremely good approximation for the process. The equality also holds if the beginning and end states are in complete equilibrium, whether or not the process is reversible, since the equilibrium conditions are state functions and do not depend on the process.

In practical terms, we speed up desired processes with interactions between the system of interest and the surroundings external to that system. Consider the special case where the processes change the state of the system from one equilibrium state to another. This situation is illustrated in figure 1.1 which describes two paths a process may take in going from equilibrium state A to equilibrium state B. Let the ordinates represent any two independent thermodynamic variables (such as pressure and temperature, or volume and temperature, or volume and entropy, etc.). Any two such variables uniquely determine the equilibrium state and thus all other variables. By definition, the system at A will remain at that state indefinitely unless a small amount of nonequilibrium is introduced from an external system - for example, the nonequilibrium introduced by forcing a gradual change of volume, or by slowly letting heat in or out of the system. In principle, the nonequilibrium could be produced by a slow change in any other variable, or a combination of variables, caused by interaction with an external system. For a change in volume, mechanical work must be done on the system or by the system to move the gas boundaries against or with the gas pressure, respectively. If this change in variable were applied infinitely slowly, the system would trace a path from A to B given by the solid curve for which every point on the curve is essentially a state in equilibrium and for which the process would stop immediately as soon as the interaction with the external system were terminated. For this path, the process is reversible and the equality of equation (1.5) would apply. Since this process would take infinitely long, as a practical matter the process would be speeded up by forcing it to follow an irreversible nonequilibrium path, say from A to A'. At A' the inequality of equation (1.5) would hold. Then, if the forcing function from the external source were removed, the system could change spontaneously from the nonequilibrium state A' to an equilibrium state B', at which point the change in the system would stop and the equality of equation (1.5) would hold so far as the internal system is concerned (i.e., not including changes in the external

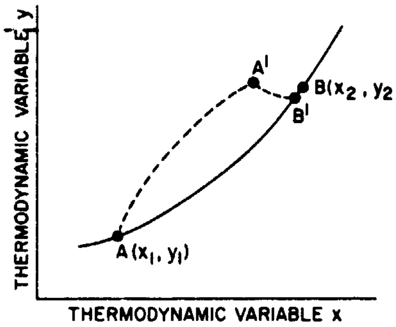

Figure 1.1.- Process paths from equilibrium state A to equilibrium state B.

system). State B' might not be exactly the same as state B if the forcing function from the external system were not terminated at the appropriate point for spontaneous internal processes to lead to B; however, B' will lie somewhere on the equilibrium line containing AB (fig. 1.1). The surface formed by all such lines in a third dimension, which represents another thermodynamic variable z, is called the *equilibrium surface*. The system could be forced back to state B by a further irreversible path if the appropriate interaction with an external system is used. For any irreversible path $AA'B$, the total entropy change of the internal and external systems will be greater than zero. Often the engineer is interested only in the balances that pertain to the internal system, which are uniquely determined by the starting and end points A and B. In other words, the internal system balance will be the same as though the path had been the reversible path, in which case, equation (1.5) may be used with the equality sign. However, note that somewhere external to the system in which a change of state has taken place, there have been changes which when coupled with the changes in the system, increase the total entropy of the system and its surroundings; otherwise the process would not have occurred in finite time.

Conservation theorems for nonequilibrium or irreversible processes in closed systems can also be deduced from relations such as equation (1.5). Consider a system kept at fixed specific volume V and entropy S. These two independent variables uniquely determine the equilibrium state of the system and therefore all remaining thermodynamic variables at equilibrium, such as E, p, T, etc. Now if the internal system undergoes an irreversible process by interacting with an external system and is then returned to its original equilibrium state, while V and S are maintained constant throughout, the integral of all changes dE must sum to zero. This can occur only if dE vanishes over each interval of the cycle. Thus internal energy is a conserved quantity in any internal process where V and S are fixed; in contrast, the quantities pressure or temperature might vary during this particular process and then return to their initial value. Similarly, V would be conserved in nonequilibrium processes that occur at fixed E and S; S would be conserved at fixed E and V.

The same relation given by equation (1.5) is conveniently expressed in terms of other thermodynamic quantities. Substituting the definition of enthalpy ($H = E + pV$) into equation (1.5), again for a closed system, one obtains

$$dH - V\,dp - T\,dS \leq 0 \tag{1.6}$$

Thus enthalpy is a conserved quantity for systems kept at constant pressure and constant entropy. Similarly, if the free energy ($F = E - TS$) is substituted into equation (1.5),

$$dF + p\,dV + S\,dT \leq 0 \tag{1.7}$$

or the free enthalpy ($G = H - TS$) into equation (1.6),

$$dG - V\,dp + S\,dT \leq 0 \tag{1.8}$$

Thus, F is a conserved quantity for closed systems constrained to fixed V and T, and becomes a minimum for these systems at equilibrium. Similarly, G is a conserved quantity for closed systems constrained to fixed p and T and becomes a minimum for these systems at equilibrium. In the laboratory, it is more convenient to keep temperature, pressure, and volume constant than entropy or energy, so the free energies are particularly useful for describing the equilibrium state in the usual experimental situation.

The thermodynamicist thinks of entropy in relation to the amount of work that can be abstracted from a system by reversible processes at constant temperature. From equation (1.7), this amount of work is just the decrease in free energy:

$$(-dF)_T = (p\ dV)_T$$

Thus, free energy F represents that part of the energy E available for work at isothermal, equilibrium conditions, while the quantity TS represents that part of E not available. Similarly, the decrease in Gibbs' free energy is the work abstracted from this system plus the decrease in the quantity pV:

$$(-dG)_T = (p\ dV)_T - d(pV)_T$$

The product pV represents the work done by 1 mol of ideal gas expanding at constant pressure from infinite density to volume V. This product is also sometimes referred to as flow work by fluid dynamicists (ref. 4).

Relations between thermodynamic variables at equilibrium and their partial derivatives are readily derived from equations (1.5) through (1.8). For example, in a closed system the pressure, volume, temperature, and entropy are, respectively

$$p = -\left(\frac{\partial E}{\partial V}\right)_S = -\left(\frac{\partial F}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_E = -S\left(\frac{\partial T}{\partial V}\right)_F \qquad (1.9)$$

$$V = \left(\frac{\partial H}{\partial p}\right)_S = \left(\frac{\partial G}{\partial p}\right)_T = -T\left(\frac{\partial S}{\partial p}\right)_H = S\left(\frac{\partial T}{\partial p}\right)_G \qquad (1.10)$$

$$T = \left(\frac{\partial E}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_p = p\left(\frac{\partial V}{\partial S}\right)_E = -V\left(\frac{\partial p}{\partial S}\right)_H \qquad (1.11)$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = -\left(\frac{\partial G}{\partial T}\right)_p = -p\left(\frac{\partial V}{\partial T}\right)_F = V\left(\frac{\partial p}{\partial T}\right)_G \qquad (1.12)$$

(Some of these relations are useful for the purpose of relating thermodynamic quantities to statistical mechanics.)

When the thermodynamic relations are known, one can, in principle, solve any fluid problem in which transport phenomena can be neglected (ref. 5) (i.e., where the effects of viscosity, conduction, diffusion, and radiation are all small). One needs to solve simultaneously, subject to the appropriate boundary conditions, equations of conservation of energy, momentum, and mass, and the equation of state, shown below in simplified one-dimensional, steady-state form:

$$de + d\left(\frac{p}{\rho}\right) + u\,du = 0 \qquad (1.13)$$

$$dp + \rho u\,du = 0 \qquad (1.14)$$

$$u\,d\rho + \rho\,du = 0 \qquad (1.15)$$

$$p = p(\rho,T) \qquad (1.16)$$

where u is the fluid velocity. Such solutions may be very difficult in general, and the fluid dynamicist's task is to find particular or approximate solutions to specific problems of interest. That small part of the problem with which this book is concerned is to express the thermodynamic quantities as functions of the appropriate variables so that such solutions are possible, in principle at least.

If the gas is in equilibrium, the case considered for the present, any two thermodynamic variables determine the complete state of the gas. As a general rule, solutions are simpler and mathematical expansions converge more rapidly if independent variables can be chosen that are relatively constant for the problem at hand. Thus, p and T are normally chosen if the process in question tends to occur at constant pressure, while ρ and T are convenient for problems where density is relatively constant, and S and T are appropriate for constant entropy processes. However, any other combination of two variables can be used If approximate thermodynamic relations can be devised which are simple enough analytically so that they can be inverted, the engineer gains flexibility in the choice of independent variables.

1.4 PHYSICAL CHEMICAL METHODS FOR OBTAINING THERMODYNAMIC QUANTITIES

Originally, thermodynamic quantities were determined by the physical chemist, who developed means of measuring p, V, T, and also Δq, the heat added to a closed system. The specific heats could then be determined experimentally:

$$C_v = \left(\frac{\Delta q}{\Delta T}\right)_v \qquad (1.17a)$$

if measurements were made in a constant volume device, or

$$C_p = \left(\frac{\Delta q}{\Delta T}\right)_p \qquad (1.17b)$$

if in a constant pressure device. Then, in the constant volume experiment, the energy and entropy could be derived by the simple numerical integrations:

$$E = \int C_v \, dT \tag{1.18a}$$

$$S = \int \frac{dq}{T} = \int \frac{C_v \, dT}{T} \tag{1.19a}$$

or, in the constant pressure experiment, enthalpy and entropy are obtained:

$$H = \int C_p \, dT \tag{1.18b}$$

$$S = \int \frac{dq}{T} = \int \frac{C_p \, dT}{T} \tag{1.19b}$$

The other thermodynamic functions are all related, by definition, to the above quantities. The constants of integration in equations (1.18) and (1.19) remain undetermined; thus, energy, enthalpy, entropy, and the free energies were all related to some arbitrary reference level (taken to be zero for a pure stable gas at standard temperature and pressure, usually $p = 1$ atm and $T = 273°$ K, though both 288° K and 293° K are also often used as standard reference temperatures). This was sufficient for many purposes where only differences such as ΔE, ΔS, or ΔF are needed to solve the problems of interest. However, Δq is difficult to measure accurately because of heat losses, truly constant pressure or constant volume processes are hard to maintain, and, in any case, there are practical limits to the range of T and p available to the experimenter. Thus, a more precise method of determining the thermodynamic properties based on measured atomic and molecular constants is now used.

According to the results of statistical mechanics, all thermodynamic properties of dilute gases can be determined from the energies ε_i and the degeneracies g_i of the unperturbed atomic or molecular states of the gas particles. Fortunately, these energy levels are known very accurately from spectrographic measurements in many cases of interest, and the degeneracies are generally known as a result of quantum mechanical interpretation and classification of spectra. The fruition of these basic disciplines now permits thermodynamic properties to be evaluated so precisely that other methods are not normally competitive.

1.5 REVIEW OF BASIC STATISTICAL MECHANICS

Statistical mechanics is based on the following postulate:

Basic Postulate of Statistical Mechanics

Spontaneous processes of a closed system always lead to a more probable state of the system as a whole. The qualification "as a whole" is included because, if a small part of the system is isolated, statistical fluctuations can occur, leading to a transient, less probable state for that part of the system. Such transient fluctuations lead to real phenomena such as Brownian motion and scattering of light from the Earth's atmosphere, for example. However, in a practical sense, the postulate is found to agree with reality for any system with dimensions large compared with the mean free path between molecular collisions or where the state properties are averages over times long compared with the mean collision time. This time irreversibility of spontaneous processes in closed systems is deduced in a sense from the Boltzmann *H*-theorem (ref. 6), which might be considered a proof of the above postulate. However, the result of the Boltzmann *H*-theorem is really introduced by the assumption made that the molecules entering collision are uncorrelated by past history (ref. 6); this assumption automatically introduces a distinction between past and future into the kinetic gas model. For purposes of this book, it seems appropriate to merely state the postulate as one that agrees with observed behavior of systems rather than attempt to prove the postulate from more fundamental principles. According to the above postulate, an equilibrium system resides in its most probable state. This maximum probability is subject to the constraints imposed on the system, such as the total volume, the pressure, the number of molecules, or the energy, etc.

A quantity W, called the thermodynamic probability, is defined as the number of equivalent ways the fundamental particles of the system can be distributed in the different states available to these particles. The quantity W is not really a probability since it is not normalized to unity, but it is proportional to the probability so that, at equilibrium, W is a maximum. In probability theory, W is called the number of permutations. One can see that W has properties similar to the entropy S, which also tends to increase as a result of spontaneous processes and become maximum at equilibrium. However, the second law of thermodynamics defines entropy as an extensive property so that the total entropy of several systems is the sum of the individual entropies

$$S = \sum_i S_i \tag{1.20}$$

whereas the total thermodynamic probability is the product of the individual thermodynamic probabilities,

$$W = \prod_i W_i \tag{1.21}$$

Consequently, S must be proportional to the logarithm of W:

$$S_i = k \ln W_i \tag{1.22a}$$

$$S = k \ln W \tag{1.22b}$$

Note that if some constant different from zero is added to equation (1.22a), a different constant then appears in the summation given by equation (1.20) and in equation (1.22b). Consequently, the constant must be zero to maintain an invariant functional relation between S and W. This fact establishes the absolute level of entropy.

Equation (1.22) constitutes a fundamental definition called the Boltzmann definition of entropy. In fact, the dimensionless quantity W could be used in place of entropy. However, the latter was defined and measured empirically long before the statistical relations were understood, so the precedent is now well established that the dimensional quantity S is used to describe the direction of spontaneous change in thermodynamic systems. Where the logarithms are taken to the base e, the proportionality constant between S and $\ln W$ must be the Boltzmann constant k to match the statistical and thermodynamic definitions of entropy.

The thermodynamic probability W is a measure of the uncertainty about the system. If the state of the system were precisely known, W would be unity and the entropy would be zero. This situation exists at absolute zero temperature for many systems. If an uncertainty exists whether the system is in any one of W equally probable states, the entropy is $k \ln W$. The larger the uncertainty in the state of the system, the larger W and the entropy become.

Strictly speaking, W should represent the total number of states available to the system. However, it will be more convenient to use W to represent a more limited quantity, namely, the total number of states of a system constrained to have a given set of occupation numbers n_i for the particles that occupy each available state i. In other words, the uncertainty in this hypothetical system arises from the exchange of like particles between states, but the distribution function for the values of n_i remains fixed. This model is useful because it allows one to define the entropy of both equilibrium and nonequilibrium systems and, for most practical purposes, it yields the same result as if the distribution function for the occupation numbers n_i were allowed to fluctuate. Real systems are in a dynamic state of fluctuation, of course, because of collisions and photon transitions, for example. Thus, in real systems, the occupation numbers n_i fluctuate about some mean value. Only the energy and the total particle number n are conserved for a system isolated from its surroundings, and the fluctuations in the occupation numbers means that a manifold of additional and equally probable states are available to the system, increasing the uncertainty about the system and therefore the entropy of the system. For this reason, many authors (refs. 7-9) prefer to define a quantity Ω as the total number of states available to the system with a given energy, to distinguish it from the quantity W representing the thermodynamic probabilities for systems constrained to single sets of occupation numbers n_i. Thus,

$$\Omega = \sum_{E=const} W \tag{1.23}$$

where the summation extends over all sets of occupation numbers which result in the given total energy. The equilibrium system is that one for which all [illegible] are equally probable, and the entropy of the equilibrium system becomes

$$S = k \ln \Omega \tag{1.22c}$$

Gibbs developed the concept of the *ensemble* to deal with problems associated with fluctuating occupation numbers. The ensemble represents a hypothetical distribution of equal energy systems, each of which can be described as a point in $6n$-dimensional phase space (three position coordinates and three momenta for each of the n particles in the system). As the particles of the system move about in physical space, the location of the system moves in phase space. The density of these system points obeys the same set of Liouville equations that determine the flow of a nonviscous fluid (refs. 10 and 11). The density of systems in the volume element about a point in phase space is proportional to the fraction of time that a real system will be found in that particular configuration with its particular set of occupation numbers n_i. A *canonical ensemble* is that particular ensemble that is steady state in time. The thermodynamic probability Ω is the total number of different configurations found in the canonical ensemble and is a constant. The quantity W is the number of member systems of the ensemble which have the same distribution function for the occupation numbers; it may be considered a fluctuating quantity that represents the thermodynamic probability of a system at a given instant of time.

The canonical ensemble is sometimes also called the *microcanonical ensemble* to distinguish it from the *grand canonical ensemble*, another concept introduced by Gibbs. The grand canonical ensemble is an ensemble of equal energy systems with all possible total numbers n allowed (whereas n is a fixed quantity in the closed systems considered so far). This ensemble is useful for treating the open systems considered in respect to chemical equilibrium in chapter 2. Although the ensemble concepts have proven very useful in deriving certain average properties of real systems (ref. 12), with the advantage of hindsight we can now derive the properties of interest without these concepts, focusing attention on a single system and using the fact that Ω can be approximated quite well by the maximum possible value of W, that is, W_{max}.

For quantitative applications, the entropy is expressed as

$$S = k\, ln\, W_{max} + k\, ln\, \frac{\Omega}{W_{max}} \tag{1.22d}$$

The first term, $k\, ln\, W_{max}$, which can be calculated with reasonable accuracy, represents the entropy of a system constrained to the most probable distribution of occupation numbers. The second term, $k\, ln(\Omega/W_{max})$, can be approximated only roughly. However, in section 1.12, we find that this term is the same order of magnitude as terms that are neglected in evaluating $k\, ln\, W_{max}$ and it represents the increase in entropy required to account for fluctuations about the most probable state. For most systems of practical interest, the number of particles is very large (typically the order of 10^{19}) and, in this case, the correction is truly negligible. Physically, this means that in systems having large numbers of particles, the fluctuations about the mean distribution are percentagewise very small!

The advantage gained by use of equation (1.22b) as the basic definition of entropy, with W defined as a variable representing the thermodynamic probability of a fictitious system constrained to a single distribution function, is that the definition can then be applied to both the equilibrium and nonequilibrium cases whenever the distribution function for the occupation numbers n_i is known or approximately known. (Again note that Ω is a constant and equation (1.22c) can be applied only to the equilibrium conditions.) This is useful, for example, when small sample systems are examined in which the entropy, as well as other thermodynamic quantities, may have sizeable fluctuations of interest. Again, the entropy can be assigned to a highly nonequilibrium system at each instant of time if the rate of change of the population numbers, $\dot{n}_i$, is known starting from some initial condition. In both the equilibrium and nonequilibrium cases, there will exist a fluctuation in occupation numbers in real systems which will require an added term in the expression for entropy; but in most practical situations, the correction will be negligible. Usually, only changes in entropy are needed, and the relatively constant correction term is superfluous in this case.

At this point, it may be helpful to include a few comments about the difference between classical and quantum particles since some confusion exists about these differences in both the literature and the classroom. Classical particles are considered to be completely distinguishable from one another by virtue of their position in space and time. Thus, for a system of n classical particles, there exist $n!$ different configurations of the particles that can lead to the same observable state of the system, namely, the configurations that arise from the $n!$ different exchanges of two like particles. The n particles in a solid-state crystal lattice intuitively seem to satisfy the requirements of distinguishability and, indeed, the solid-state crystal can be modeled very well by use of the classical particle concept. In gases, the distinguishability of the particles seems less obvious. The particles are free to move about and exchange position, but, in principle, according to classical mechanics the positions and momenta of all particles of the system are known at any future time if the initial conditions are given. In this sense, the classical particles are distinguishable even though the labor involved in keeping track of the huge number of particles involved in normal systems would be prohibitive, even for modern computers. However, Gibbs and other early thermodynamicists found that when all $n!$ states of such a gas were considered distinguishable, the entropy obtained statistically was too large. A nonvanishing zero level entropy was derived which led to the famous Gibbs paradox: the total entropy of such a system did not equal the sum of the entropies of its parts, as required of an extensive property (see eqs. (1.20) and (1.22)). The answer to this paradox was forthcoming only when quantum theory was developed. Strictly speaking, all particles obey quantum mechanics; classical behavior is merely a limiting behavior that is approached in certain cases, as for the highly localized particles in the solid, but it is not approached in others, as for the free particles in gases.

In quantum mechanics, the probability that a particle i will be found in a volume element of space, $dx_i\, dy_i\, dz_i$, is given by the product of the volume element and the square of the particle's wave function $\psi_i^2(x_i,y_i,z_i)dx_i\, dy_i\, dz_i$ (ref. 13). These wave functions are discussed in detail in chapter 3 and thereafter; for the present, it is sufficient to point out that if a system of n identical particles exists in which the particles are isolated (as in a solid), the individual particle wave functions do not overlap and the particles can then be treated as distinguishable. If, on the other hand, the particles are free to occupy the same region of space (as in a gas), the individual particle wave functions all overlap one another and the particles must then be treated as indistinguishable. Then the $n!$ exchanges of particles must be considered to result in the same identical state. Mathematically, this situation is modeled by expressing the wave function for the entire system of *isolated* (distinguishable) particles as the product of all one-particle wave functions (see section 4.7):

$$\psi(q_1,q_2,\ldots,q_n) = \prod_{i=1}^{n} \psi_i(q_i) \tag{1.24}$$

There are $n!$ different wave functions of this type, corresponding to all possible exchanges of the coordinates of two like particles. (Note that q_i represents three coordinates in physical space, and that the system wave function is a function of all $3n$ space coordinates.) On the other hand, the wave function for a system of (indistinguishable) particles with *overlapping* wave functions must be expressed as a determinant (again see section 4.7):

$$\psi(q_1,q_2,\ldots,q_n) = \begin{vmatrix} \psi_1(q_1) & \psi_2(q_1) & \cdots & \psi_n(q_1) \\ \psi_1(q_2) & \psi_2(q_2) & \cdots & \psi_n(q_2) \\ \psi_1(q_3) & \psi_2(q_3) & \cdots & \cdot \\ \vdots & & & \vdots \\ \psi_1(q_n) & & & \psi_n(q_n) \end{vmatrix} \tag{1.25}$$

which already accounts for all possible interchanges of two like particles. The point is that this function represents a *single* state of the system, not $n!$ states. Molecules in a gas behave as free particles and, as shown in chapter 3, free-particle wave functions extend throughout the entire available volume. Thus, the gas particle wave functions are all overlapping and the total wave function for a gaseous system of particles must be represented by a function of the form of equation (1.25). The solid, on the other hand, can be adequately modelled by $n!$ different functions of the form of equation (1.24). In a liquid, the particles are neither strictly localized nor free; this situation is more difficult to model than the limiting cases that represent the solid and gaseous states, but the wave function will obviously have the character of a product of lower rank determinants that represent the wave functions of small clusters of nearly indistinguishable particles. The number of different states of a liquid system provided by interchanging these cluster groups is much greater than unity but smaller than $n!$. Similar considerations are necessary when one corrects the idealized gas model to account for high-density effects that lead to slow diffusion of gas particles and, in effect, some localization of the particles. Again, at high temperatures, the diffusion effect in solids leads to some overlapping of single-particle wave functions and some indistinguishability of the particles.

1.6 SOLID-PHASE STATISTICS

The gas phase is of primary concern here, but it will nevertheless be instructive to consider first a system of n *localized* and therefore *distinguishable* particles (as in the solid phase). Subsequently, in the gas phase system considered, the particles are all *free to occupy the total volume* and are therefore *indistinguishable*. By this procedure, certain important differences between these two cases can be noted.

The number of ways n *distinguishable* particles can be chosen to occupy the available states k, with a given set of occupation numbers n_k, is the thermodynamic probability

$$W = n! \prod_k \frac{1}{n_k!} \tag{1.26}$$

(Derivations of the mathematical expressions used for W are presented in references 10, 11, and 14 among others; appendix 1-A presents a brief review of these derivations.)

Systems of interest often have a number of states with the same energy level ε_i, and the number of such states is called the degeneracy of that level g_i. In this case, it is convenient to express the distribution function in terms of the numbers of particles n_i that occupy each level i. The thermodynamic probability for the solid phase system is then expressible as

$$W = n! \prod_i \frac{g_i^{n_i}}{n_i!} \tag{1.27}$$

If Stirling's approximation for the logarithm of factorials of large numbers (refs. 10, 11, and 15)

$$\ln n! \simeq n \ln n - n + \frac{1}{2} \ln 2\pi n \tag{1.28}$$

is used with equation (1.27), an approximate expression for $\ln W$ is

$$\ln W \simeq n \ln n - n + \frac{1}{2} \ln 2\pi n - \sum_i \left(n_i \ln \frac{n_i}{g_i} - n_i + \frac{1}{2} \ln 2\pi n_i \right) \tag{1.29}$$

Not all the numbers n_i are so large that Stirling's approximation is justified. However, the total number of particles in the system may be taken so large that the approximation is fully justified for all cells that contribute appreciably to the total thermodynamic probability W. In fact, if only terms of orders n and n_i are retained:

$$\ln W \simeq n \ln n - \sum n_i \ln \frac{n_i}{g_i} \tag{1.30}$$

The neglected terms are self-compensating for the small occupation numbers so the results are the same as those given by the more rigorous derivation of Darwin and Fowler using the method of steepest descent (refs. 16 and 17).

The values of n_i are subject to the restriction that the total number of particles be fixed:

$$n - \sum_i n_i = 0 \tag{1.31}$$

and that the total energy be some finite constant E,

$$E - \sum_i \varepsilon_i n_i = 0 \tag{1.32}$$

At this point, Lagrange's method of undetermined multipliers is used (refs. 11, 14, and 15) to maximize W, subject to the above constraints. Equations (1.31) and (1.32) are multiplied by arbitrary constants and added equation (1.30). The derivative of this sum with respect to n_i must be zero for all n_i when W is an extremum subject to the given restrictions. The constant multipliers are designated here by $(\alpha - 1)$ and β, respectively, merely to put the final results in the traditional form. Then

$$\frac{\partial\, ln\, W}{\partial n_i} + (\alpha - 1)\frac{\partial}{\partial n_i}\left(n - \sum_j n_j\right) + \beta\frac{\partial}{\partial n_i}\left(E - \sum_j \varepsilon_j n_j\right) = 0 \tag{1.33}$$

From equations (1.30) and (1.33), the most probable distribution of occupation numbers is found to be

$$n_i = g_i\, e^{-(\alpha+\beta\varepsilon_i)} \tag{1.34}$$

the general form of the Maxwell-Boltzmann distribution. The constant α is just a normalization factor that equates the sum of all n_i to the total number n, as required by equation (1.31),

$$= \sum_i n_i = e^{-\alpha} \sum_i g_i\, e^{-\beta\varepsilon_i} \tag{1.35}$$

The summation on the right-hand side of equation (1.35) is called the *partition function*, designated here by the sumbol Q:

$$Q = \sum_i g_i\, e^{-\beta\varepsilon_i} \tag{1.36}$$

The partition function is particularly important because all equilibrium thermodynamic properties of a system of particles can conveniently be derived from it.

In terms of the partition function, the Maxwell-Boltzmann distribution, equation (1.34), can be expressed as

$$n_i = \frac{n}{Q} g_i e^{-\beta\varepsilon_i} \tag{1.37}$$

and the total energy of the system by

$$E = \sum_i \varepsilon_i n_i = \frac{n}{Q} \sum_i \varepsilon_i g_i e^{-\beta\varepsilon_i} \tag{1.38}$$

while the thermodynamic probability according to equation (1.30) is given by

$$\begin{aligned} \ln W &\simeq n \ln n - \frac{n}{Q} \sum_i g_i e^{-\beta\varepsilon_i} (\ln n - \ln Q - \beta\varepsilon_i) \\ &\simeq n \ln Q + \beta E \end{aligned} \tag{1.39}$$

Then the entropy of a solid-state system or a system of distinguishable particles is

$$S = k \ln W = nk \ln Q + k\beta E \tag{1.40}$$

If each state were treated separately with a degeneracy $g = 1$, the same results would be obtained. For example, the partition function and the Maxwell-Boltzmann distribution could then be collapsed from a sum over all different states k to a sum over all different energy levels i:

$$Q = \sum_k e^{-\beta\varepsilon_k} = \sum_i \left(\sum_{\substack{k=1 \\ \varepsilon_k = \varepsilon_i}}^{g_i} e^{-\beta\varepsilon_k} \right) = \sum_i g_i e^{-\beta\varepsilon_i} \tag{1.36a}$$

$$n_i = \sum_{\substack{k=1 \\ \varepsilon_k = \varepsilon_i}}^{g_i} n_k = g_i n_k = \frac{n}{Q} g_i e^{-\beta\varepsilon_i} \tag{1.37a}$$

with results identical to those given before in equations (1.36) and (1.37).

The partition function, often designated by the symbol Z rather than Q, is sometimes called the *state sum* or Zustandssumme. The term state sum originally indicated a summation over only the internal states of the particle, whereas the partition function includes a summation over both internal and kinetic energy states. Here the term state sum is reserved for a somewhat different concept to avoid an ambiguity that often appears in the literature between the partition function and the state sum as defined here. The *partition function* is the sum over all states available to each particle that is a member of the system; the *state sum* is the sum over all states available to each system that is a member of an ensemble of systems in which the total system energy E can take all possible values. This state sum is designated here by Q_n to call attention to both its difference and its relation to the partition function Q:

$$Q_n = \sum_{j=1}^{\infty} e^{-\beta E_j} \tag{1.41}$$

Often we have a situation where the individual particle energies are independent of one another, in which case the total energy may be expressed as

$$E_j = \sum_{k=1}^{n} \varepsilon_k \tag{1.42}$$

where the summation extends over all n particles residing in the various states with energy ε_k. Thus

$$Q_n = \sum_{j=1}^{\infty} e^{-\beta \sum_{k=1}^{n} \varepsilon_k} = \sum_{j=1}^{\infty} \prod_{k=1}^{n} e^{-\beta \varepsilon_k} \tag{1.43}$$

The sum over all j includes every possible state k of every particle, so we may factor out n identical quantities Q:

$$Q_n = \prod_{k=1}^{n} Q = Q^n \tag{1.44}$$

where the Q terms are the single-particle partition functions defined previously. The thermodynamic properties of a system may all be expressed in terms of the state sum Q_n as well as of the partition function; for example,

$$\ln W \simeq \ln Q_n + \beta E \tag{1.39a}$$

$$S \simeq k \ln Q_n + k\beta E \tag{1.40a}$$

The relation between the state sum and the partition function given above is valid for distinguishable particles only; the product Q^n includes all $n!$ exchanges between like particles in the system. For gas phase where the particles must be treated as indistinguishable, the state sum is identified with $Q^n/n!$.

1.7 GAS PHASE STATISTICS

Gas phase differs from solid phase in that all particles are free to occupy the entire volume and, for a pure phase, the particles are identical and therefore indistinguishable from one another. This indistinguishability changes the statistics since the $n!$ permutations of the n particles with one another represent a single observable state of the system. Thus, the thermodynamic probability, that is, the total number of different ways the particles can occupy the available energy levels i with a given set of occupation numbers n_i, becomes

$$W = \prod_i \frac{g_i^{n_i}}{n_i!} \tag{1.45}$$

in place of equation (1.27), the solid-state relation.

One might object that equation (1.45) could be less than unity if occupation numbers n_i were much larger than the available degeneracies g_i. However, the particles are so far apart in the gas phase that the degeneracies of available kinetic energy states (derived in ch. 3) are much larger than the number of particles available to fill them. This means that the most probable occupation numbers in any single state are 0 and 1. One immediately sees the advantage gained in summing over energy levels with large degeneracies rather than summing over all states with degeneracy one; the occupation numbers n_i can then become large enough that Stirling's approximation can be used for the factorial quantities. Also, since the g_i are much larger than the n_i, one can see that W is indeed larger than unity. The logarithm of W for gas phase systems is

$$ln\ W = \sum_i (n_i\ ln\ g_i - ln\ n_i!) \tag{1.46}$$

which, with Stirling's approximation, becomes

$$\begin{aligned} ln\ W &\approx -\sum_i \left(n_i\ ln\ \frac{n_i}{g_i} - n_i + \frac{1}{2}\ ln\ 2\pi n_i\right) \\ &\approx n - \sum_i n_i\ ln\ \frac{n_i}{g_i} \end{aligned} \tag{1.47}$$

where again only terms of order n_i are retained in the last expression above. Except for the constant term, the functional relation between W and n_i is the same as in equation (1.30) and leads to the same form for the Maxwell-Boltzmann distribution as before, equation (1.37). Also, the total energy of the system is again given by equation (1.38). However, the thermodynamic probability now has a slightly different relation to the partition function Q:

$$\begin{aligned} ln\ W &\approx n - \frac{n}{Q}\sum_i g_i\ e^{-\beta\varepsilon_i}(ln\ n - ln\ Q - \beta\varepsilon_i) \\ &\approx n - n\ ln\ n + n\ ln\ Q + \beta E \\ &\approx n\ ln\ \frac{Q}{n} + \beta E + n \end{aligned} \tag{1.48}$$

and the entropy of a gas phase system of particles is

$$S = k \ln W = nk \ln \frac{Q}{n} + k\beta E + nk \tag{1.49}$$

This appears to be somewhat similar to the expression for entropy of a solid-state system of particles given by equation (1.40), except for the constant $-nk(\ln n - 1)$. However, this constant is very important in establishing reference levels for the free energies and the criteria for chemical equilibrium in the gas phase. Classical thermodynamics alone was unable to establish a unique reference level of entropy, and a major contribution of statistical mechanics and quantum mechanics is that an absolute value of entropy is provided. The reader can readily sense that the expression for entropy of a liquid phase system is something intermediate between equations (1.40) and (1.49), representing a case in which the particles are neither strictly localized nor free. Strictly speaking, the above models are not entirely precise for the solid-state and gas phases either. In solid state, atoms can diffuse through the crystal lattice and interchange with one another, leading to a certain degree of indistinguishability of the particles. Similarly, diffusion is slow in very dense gases leading to a certain degree of distinguishability of the particles according to their position. However, these effects can be treated most easily by considering them to be perturbations on the idealized models presented previously rather than attempting to work from a more exact model at the start.

At first glance, one might think that the entropy of a gas is less than that of a solid because of the large negative factor $-nk(\ln n - 1)$ added to the expression for gases, equation (1.49). However, this is not the case; the available degeneracies in the gas are so much larger than in the solid phase that the entropy increases by a large amount when a solid system of n particles is vaporized. This agrees with our intuitive sense that the uncertainty in the state of a system is greatly increased as it transforms from the solid to the vapor phase.

Just as for solids, the thermodynamic probability W, entropy S, and other thermodynamic properties of gas phase can be related to the state sum Q_n in place of the single-particle partition function Q. However, in this case,

$$Q_n = \frac{Q^n}{n!} \tag{1.50a}$$

$$\ln Q_n = n \ln Q - n \ln n + n \tag{1.50b}$$

and the expressions for W and S become

$$\ln W = \ln Q_n + \beta E \tag{1.48a}$$

$$S = k \ln Q_n + k\beta E \tag{1.49a}$$

which are identical to the expressions derived for the solid-state system. In this sense, the state sum Q_n is a somewhat more universal parameter than the single-particle partition function Q.

Because of the confusion that exists between the partition function Q and the state sum Q_n, the statistics of gas phase are sometimes treated as though the particles are classical and therefore distinguishable, leading to the same expressions as for the solid phase. Then, the single-particle partition function Q is shown to be proportional to the available volume (as in ch. 3) and the argument is made that the free volume per particle is the total volume V divided by the total number of particles n. The rationale given for this assumption is that V/n is the average volume available which is free of perturbation from neighboring particles and that collisions with the neighboring particles limit the number of free-particle momentum states that should be counted in evaluating the degeneracies g_i. This limitation of the free volume introduces the additional factor n^{-1}, which leads to the same results obtained above, where the gas was modelled as a collection of particles free to move without perturbation throughout the entire volume V. Although collisions with other particles inhibit some of the momentum states available in a gas system of particles, the mean free path between collisions is known to be much larger than $(V/n)^{1/3}$. Thus putting the gas particles in potential boxes of size V/n is physically unrealistic, even though the results obtained with this model are valid.

The remaining thermodynamic properties of a system can now be derived from the foregoing results for the thermodynamic probability, the distribution function, and the entropy. However, we digress for the moment to discuss classical analogs to the Maxwell-Boltzmann distribution, to the partition function and the state sum, and to evaluate β in terms of temperature.

1.8 CLASSICAL STATISTICAL MECHANICS

The Maxwell-Boltzmann distribution expressed in integer form, equation (1.34), is obviously appropriate for quantum particles where one needs to sum over discrete or quantized states. However, these states often lie close together and can conveniently be treated as a continuum, in which case the equivalent classical integrals for the partition function and the state sum are appropriate. In fact, the integration is often easier to perform than the summation. In such integrations, a quantum energy state i corresponds to a volume element of classical phase space $dp\,dq$, which is a shorthand notation for a product such as $dp_x\,dp_y\,dp_z\,dx\,dy\,dz$, involving all momenta and coordinates available to the particle. The Maxwell-Boltzmann distribution of equation (1.34) may thus be expressed in differential form as

$$\rho = \frac{dn}{dp\,dq} = \frac{n}{Q}\,e^{-\beta H(p,q)} \tag{1.51}$$

where ρ represents the density of the distribution in particle phase space and $H(p,q)$ is the energy of the particle, in general a function of all the particle coordinates q and momenta p. The constant multiplier n/Q has already been chosen to normalize the integral of all dn to the total number of particles n, where the quantity Q is the *phase integral*:

$$Q = \iint e^{-\beta H(p,q)} dp\, dq \tag{1.52a}$$

which is the classical analog to the partition function. The integrations are performed over all the coordinates and momenta available to the particle, which may be a sizeable number if the particle is a polyatomic molecule. For a single structureless particle, the integral is sixfold, corresponding to three independent coordinates and three independent momenta. The degeneracy g does not appear because states with the same energy are automatically counted when integrating over all coordinates and momenta, which is equivalent to setting the degeneracy g to unity and summing over all states to obtain the partition function (as in the first expression of eq. (1.36a)).

One difference between the phase integral and the partition function remains; equation (1.52a) is a dimensional quantity and the value of the integral depends on the units chosen for the coordinates and momenta; the partition function, on the other hand, is dimensionless. Before the advent of quantum theory, there was no way to choose one set of units over another, and Gibbs had no choice but to leave the phase integral in the form of equation (1.52a). In fact, the classical relations could be expressed equally well in terms of velocities and coordinates rather than momenta and coordinates. The latter were chosen here with the advantage of hindsight provided by the Heisenberg uncertainty principle (see ch. 3), which shows that a single state of the particle includes a region of phase space with the size

$$dp_i\, dq_i = h \tag{1.53}$$

where h is the Planck constant. *This* establishes the relation between units that must exist so the phase integral quantitatively agrees with the partition function. Thus Q is written in dimensionless form as

$$Q = \frac{1}{h^f} \iint e^{-\beta H(p,q)} dp\, dq \tag{1.52b}$$

where f, the number of degrees of freedom, is defined as the number of independent sets of space and momentum coordinates that appear in the energy function H.

The choice of the particular set of coordinates and momenta used remains arbitrary because the best choice, dependent on the functional form of the energy $H(p,q)$, is that set which permits the integral to be evaluated most easily. For the free particles treated in chapter 3, the Cartesian coordinate set is most convenient, for example

$$Q = \frac{1}{h^3} \iiiint\!\!\iint e^{-\beta H(p_x,p_y,p_z,x,y,z)} dp_x\, dp_y\, dp_z\, dx\, dy\, dz \tag{1.52c}$$

But other coordinate sets, such as cylindrical coordinates or spherical coordinates, for example, may be required for different problems. The appropriate sets are called *conjugate momenta and coordinates* and the units of each must be chosen so that their products equal the Planck constant. The energy function must be expressed in terms of a conjugate set, and when thus expressed it is called the *Hamiltonian*. A conjugate set of momenta and coordinates p_i, q_i is a set that puts the Hamiltonian differential equations of motion in *canonical form*, namely,

$$\frac{\partial H}{\partial q_i} = -\frac{dp_i}{dt}, \qquad \frac{\partial H}{\partial p_i} = \frac{dq_i}{dt} \tag{1.54}$$

Usually, the coordinate system is chosen first so that it conveniently fits the boundary conditions of the problem at hand, thereby simplifying the mathematics. The conjugate momenta for these coordinates are then found according to the following recipe:

1. The Lagrangian function L, the difference between the kinetic energy T and the potential energy V, is expressed in terms of the chosen coordinates and their first derivatives with respect to time as

$$L(q_i,\dot{q}_i) = T(q_i,\dot{q}_i) - V(q_i) \tag{1.55}$$

2. The momentum p_i, which is conjugate to q_i, is simply the partial derivation of L with respect to $\dot{q}_i$:

$$p_i = \frac{\partial L}{\partial \dot{q}_i} \tag{1.56}$$

3. The time derivatives $\dot{q}_i$ are determined as functions of the conjugate sets p_k and q_k from the inverse relation to equation (1.56).

4. Finally, the Hamiltonian is expressed as a function of just the conjugate set of coordinates and momenta:

$$H(p,q) = \sum_i p_i\dot{q}_i(p_k,q_k) - L[\dot{q}_i(p_k,q_k),q_i] \tag{1.57}$$

The derivation that equation (1.57) is indeed the total energy $T + V$ and that the equations of motion take the form of equation (1.54) may be found in standard texts on mechanics and quantum mechanics (e.g., refs. 13 and 18).

In many cases, the Hamiltonian function can be formulated by inspection, and one need not resort to the recipe above. In more complex cases, following the recipe may be the best way to keep track of all the terms involved. Of course, once the phase integral has been set up in terms of the conjugate coordinates and momenta, the same value of the integral may be found by any equivalent transformation of coordinates. For example, it is often convenient to change momentum-space coordinates to energy-space coordinates. Then the degeneracy of states having the same energy is simply the absolute magnitude of the Jacobian for the transformation

$$dp\ dq = \left|J\left(\frac{p,q}{H,q}\right)\right| dH\ dq \tag{1.58}$$

In the absence of external or intermolecular forces, the energy of the gas molecule is independent of the space coordinates (such as x, y, and z). Integrating over these coordinates then simply yields the available volume V. Thus a relation valid for dilute gases in the absence of external forces is

$$\frac{Q}{n} = \frac{V}{nh^3}\iiint e^{-\beta H(p_x,p_y,p_z)}dp_x\ dp_y\ dp_z \tag{1.59}$$

Note that for gases (Q/n) is the quantity on which the thermodynamic probability W and the entropy S depend (eqs. (1.48) and (1.49)). Thus the appropriate volume that enters these definitions is the free volume per molecule, V/n. If V is the molar volume, then the appropriate number of molecules is the Avagadro number N.

A *γ-space phase integral* (also used in the literature) is the classical analog to the state sum as defined previously; γ-space is the $6n$-dimensional space in which the ensemble is treated; each system in the ensemble is described by a point in γ-space. The Hamiltonian of such a system is generally a function of all $6n$ momenta and space coordinates available to the n particles of the system, and the γ-space phase integral may be expressed as

$$Q_n = \frac{1}{n!h^{3n}}\int\ .\ .\ .\int e^{-\beta H(p,q)}dp_1\ dp_2\ .\ .\ .\ dq_{3n} \tag{1.60}$$

Note that the factor $n!$ is included in the denominator to account for the interchangeability of the particles, without changing the state of the system (see section 1.5). If, and only if, the Hamiltonian can be expressed as a sum of independent single-particle energies, all with the same functional form $\varepsilon(p_i,q_i)$:

$$H(p,q) = \sum_{i=1}^{n} \varepsilon(p_i,q_i) \tag{1.61}$$

then the integral can be decomposed into n identical, single-particle phase integrals Q:

$$Q_n = \frac{1}{n!h^{3n}}\left[\iint e^{-\beta\varepsilon(p_i,q_i)}dp_i\ dq_i\right]^n = \frac{Q^n}{n!} \tag{1.62}$$

The γ-space phase integral is convenient to use later (ch. 8) to analyze the corrections to ideal gases required to account for particle interactions.

1.9 EVALUATION OF β

The constant β determines the total energy in accord with equation (1.38). If the results of kinetic theory are assumed to be established, β can be evaluated simply by considering the special case where ε is just the kinetic energy of a free particle, namely, $(p_x^2 + p_y^2 + p_z^2)/2m$. Expressing the momenta in terms of the velocities ($p_x = m\dot{x}$, etc.), one finds a differential form of the distribution function, equation (1.51),

$$dn = n\left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-(\beta m/2)(\dot{x}^2+\dot{y}^2+\dot{z}^2)}d\dot{x}\ d\dot{y}\ d\dot{z} \qquad (1.63)$$

where the normalization is already adjusted to n molecules per unit volume. Equation (1.63) is just the familiar Maxwell-Boltzmann velocity distribution given by the kinetic theory of gases (ref. 11) and, by a comparison of terms,

$$\beta = \frac{1}{kT} \qquad (1.64)$$

Other ways can be devised to evaluate β. For example, if the ideal gas law is accepted as an experimentally proven relation for dilute gases, the pressure of gas particles in a Maxwell-Boltzmann distribution can be calculated as a function of β and equated to the ideal gas value nkT. The details are left as problem 1.1.

Problem 1.1: Determine the pressure of a dilute gas (zero interaction energy between molecules) by calculating the flux of the normal component of momentum over a unit surface for the distribution given by equation (1.63). Show that $p = n/\beta$; thus β must equal $(kT)^{-1}$ if the perfect gas law is accepted as valid for dilute gases.

The significance of β does not depend on the restricted nature of the problem considered above and equation (1.64) is a general relation. In fact, the quantity β would serve to characterize the state of a gas just as well as T, but we have grown so accustomed to thinking in terms of temperature, that it is well to continue to express thermodynamic relations as functions of this parameter.

The average kinetic energy per molecule for the distribution of equation (1.63) is

$$\begin{aligned}\bar{\varepsilon}_k &= \int\frac{\varepsilon dn}{n} = \left(\frac{\beta m}{2\pi}\right)^{3/2}\iiint\frac{m}{2}\,(\dot{x}^2+\dot{y}^2+\dot{z}^2)e^{-(\beta m/2)(\dot{x}^2+\dot{y}^2+\dot{z}^2)}d\dot{x}\ d\dot{y}\ d\dot{z}\\ &= \frac{3}{2\beta} = \frac{3kT}{2} \qquad (1.65)\end{aligned}$$

Thus, a fundamental definition of temperature is a quantity proportional to the average kinetic energy of the molecules in a gas, when their individual kinetic energies are distributed in a Maxwell-Boltzmann relation. Normally, one need not consider other distributions for the kinetic energies in gases since the collision-induced relaxation to the Maxwell-Boltzmann distribution of velocities is very rapid, the order of the mean collision time. However, nonequilibrium distributions will often be encountered in connection with internal energy states, which may be out of equilibrium with the kinetic modes of energy.

The internal energy of a gas molecule is normally independent of the kinetic energy of the molecule, and the velocity and internal energy coordinates are then separable. In this case, the total molecular energy may be expressed as

$$\varepsilon = \frac{m}{2}\left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2\right) + \varepsilon_{int} \tag{1.66}$$

where ε_{int} represents the rotational, vibrational, and electronic energies of the molecule. Then the integration over internal energy coordinates in equation (1.51) yields identical factors in the numerator and the denominator. Thus the average kinetic energy has the same form as equation (1.65), and T retains its significance as a measure of this kinetic energy, whether other modes of energy are available to the molecule or not. The following problems are designed to convey the concept that a mixture of gases in complete equilibrium can have only one temperature, and that a separate temperature-like quantity can be used to characterize each mode of energy frozen out of equilibrium, that is, each mode for which energy does not exchange readily with kinetic energy.

Problem 1.2: Show that, for a mixture of different gases in complete equilibrium, only one factor β appears in the derivation of the most probable distribution. It follows that the same temperature applies to all components of the gas.

Problem 1.3: Show that, if a gas is frozen in a state out of equilibrium, the number of independent Lagrange multipliers β_k needed to describe the most probable state of the gas is the number of modes of energy, or combinations of modes, in which energy is conserved (frozen). These constants are often regarded as temperatures, or pseudo-temperatures, that would describe the kinetic energy of the gas if it were in equilibrium with the internal energy mode in question. Note that the most probable distribution of internal energy is still Boltzmann in form, even though it may be restrained from reaching equilibrium with the kinetic energy mode.

1.10 EQUIPARTITION OF ENERGY

One of the important consequences of the Maxwell-Boltzmann law is the equipartition of energy. The statement is often made that, at equilibrium, $(1/2)kT$ is the average energy per molecule in each degree of freedom. Equation (1.65) is a special case that illustrates this result for three degrees of freedom. However, this statement is not general enough to be satisfactory. For example, it is somewhat troublesome to explain why a harmonic oscillator should have two degrees of freedom, when only motion in one direction is involved. The reason is, of course, that the harmonic oscillator has a potential energy mode associated with its position coordinate as well as a kinetic energy mode associated with its momentum; therefore, two degrees of freedom are associated with each direction of motion in this case rather than one degree of freedom with each direction of motion as for the particle in potential free space. A more general statement of the equipartition principle that clearly defines the meaning of a participating degree of freedom is as follows:

Theorem: If the energy H becomes infinite at the limit of each of the sets of conjugate coordinates q_i and momenta p_j, then at equilibrium,

$$\overline{q_i \frac{\partial H}{\partial q_i}} = \overline{p_j \frac{\partial H}{\partial p_j}} = kT \tag{1.67a}$$

To prove this theorem, let $q_i = q_1$. Then, from the differential form of the Boltzmann distribution, equation (1.51), the average value of $q_1(\partial H/\partial q_1)$ is

$$\overline{q_1 \frac{\partial H}{\partial q_1}} = \frac{1}{Q}\int . . . \int q_1 \frac{\partial H}{\partial q_1} e^{-H/kT} dq_1 . . . dp_r \tag{1.67b}$$

The integral can be written as

$$\overline{q_1 \frac{\partial H}{\partial q_1}} = -\frac{kT}{Q}\int . . . \int q_1 \frac{\partial}{\partial q_1}\left(e^{-H/kT}\right) dq_1 . . . dp_r \tag{1.67c}$$

which can be integrated by parts over q_1 to give

$$\overline{q_1 \frac{\partial H}{\partial q_1}} = -\frac{kT}{Q}\left(\int . . . \int \left| q_1 e^{-H/kT}\right|_a^b dq_2 . . . dp_r - \int . . . \int e^{-H/kT} dq_1 . . . dp_r\right) \tag{1.67d}$$

The first term vanishes if H becomes infinite at the limits a and b (these limits are ±∞ in Cartesian coordinates). The integral in the second term just cancels the phase integral Q so that, as stated by the theorem,

$$\overline{q_1 \frac{\partial H}{\partial q_1}} = kT \tag{1.67e}$$

The same result holds for any of the q_i or p_j terms.

Typically, the first-order terms in molecular energy are quadratic in momenta and coordinates. In the most general case, let l and m be the number of different momenta and coordinates, respectively, involved in the quadratic terms:

$$H = \sum_{i,j=1}^{l} a_{ij} p_i p_j + \sum_{i,j=1}^{m} b_{ij} q_i q_j + V(p_{l+1} . . . p_r, q_{m+1} . . . q_r) \tag{1.68a}$$

The coefficients a_{ij} and b_{ij} are constants or functions of the remaining coordinates $p_{l+1}, . . . p_r, q_{m+1} . . . q_r$. For generality, a term V that is not quadratic in these remaining coordinates is included. The sums are homogenous functions of order 2, so Euler's theorem (ref. 15) can be applied to transform the energy expression to

$$H = \frac{1}{2}\sum_{i=1}^{l} p_i \frac{\partial H}{\partial p_i} + \frac{1}{2}\sum_{j=1}^{m} q_j \frac{\partial H}{\partial q_j} + V \qquad (1.68b)$$

Taking the average value of both sides and using equation (1.67e), one obtains

$$\overline{H} = (l + m)\frac{kT}{2} + \overline{V} \qquad (1.69)$$

In many practical cases, the value of $\overline{V}$ is zero or nearly so, but it has been included here to alert the reader to the fact that this term can appear. In any case, each coordinate and each momentum that appears only in squared terms in the expression for H contributes $(1/2)kT$ to the average energy per molecule at equilibrium. Note that the number of squared terms does not matter, but the number of *independent* coordinates involved in these terms determines the multiple of $kT/2$ contributed to the average energy. With this derivation in mind, the principle of equipartition of energy can be applied in more than just a cookbook fashion.

1.11 DERIVATION OF THERMODYNAMIC PROPERTIES FROM THE PARTITION FUNCTION

From this point on, the total number of molecules n is taken to be equal to the Avagadro number N, the total free volume accordingly is the molar volume V and extensive properties are evaluated for 1 mol of gas.

The energy per mol is, according to equation (1.38),

$$E = \frac{N}{Q}\sum_i \varepsilon_i g_i\, e^{-\beta\varepsilon_i} \qquad (1.70)$$

Note that, even at absolute zero T, there can be a finite particle energy, called the *zero point energy* ε_o. For example, this might be the energy connected with nuclear structure, or dissociation, or ionization of the particles involved. Although rather high temperatures, up to 10^5 °K, are of interest here, these temperatures are still relatively low for the purpose of populating even the lowest-lying excited nuclear energy levels. Thus, for practical purposes, the nuclear energy may be considered a constant over the temperature range of interest here, and the value zero is conventionally assigned to this constant. However, dissociation and ionization energy of certain atoms and ionic particles must be accounted for by absorbing these energies into the zero point energy ε_o. Also, vibrating molecules have a zero point energy, $(1/2)h\nu$, (as discussed in ch. 5). Then equation (1.35) takes the form

$$N = e^{-\alpha}\, e^{-\beta\varepsilon_o}\sum_i g_i\, e^{-\beta(\varepsilon_i-\varepsilon_o)} \qquad (1.71)$$

and the energy per mol becomes

$$E = \frac{N\sum_i(\varepsilon_i - \varepsilon_o)g_i\, e^{-\beta(\varepsilon_i-\varepsilon_o)}}{\sum_i g_i\, e^{-\beta(\varepsilon_i-\varepsilon_o)}} + N\varepsilon_o \tag{1.72a}$$

If the symbols ε_i are understood to represent the energies measured relative to the zero point energy ε_o, then equation (1.72a) takes the same form as equation (1.70) except that the zero point energy per mol $N\varepsilon_o$ or E_o is included:

$$E - E_o = \frac{N}{Q}\sum_i \varepsilon_i g_i\, e^{-\beta\varepsilon_i} \tag{1.72b}$$

Now if the degeneracies are independent of β, we see by inspection that the energy can simply be equated to a total differential of $ln\ Q$:

$$E - E_o = -N\,\frac{d\ ln\ Q}{d\beta} \tag{1.73a}$$

or, in terms of temperature,

$$E - E_o = RT^2\,\frac{d\ ln\ Q}{dT} \tag{1.73b}$$

where R is the universal gas constant, Nk. Equations (1.73) give the relation between the energy and the partition function for a solid-phase system of localized distinguishable particles. However, for the gas phase system of indistinguishable particles, the degeneracy of the kinetic energy modes is a function of volume, which, in turn, is a function of β and pressure p. In fact, for ideal or dilute gases, where the intermolecular interactions are negligible, we found from partial integration of the phase integral, equation (1.59), that the partition function is proportional to volume. Thus, the energy of a gas must be equated to a partial derivative of $ln\ Q$ taken at constant volume:

$$E - E_o = -N\left(\frac{\partial\ ln\ Q}{\partial\beta}\right)_v = RT^2\left(\frac{\partial\ ln\ Q}{\partial T}\right)_v \tag{1.74}$$

The specific heat at constant volume is thus

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v = \frac{\partial}{\partial T}\left[RT^2\left(\frac{\partial\ ln\ Q}{\partial T}\right)_v\right] \tag{1.75}$$

The entropy may be found by integrating equation (1.75):

$$S - S_o = \int_0^T \frac{C_v\, dT}{T} = \int_0^T \frac{1}{T}\,\frac{\partial}{\partial T}\left[RT^2\left(\frac{\partial\ ln\ Q}{\partial T}\right)_v\right] dT \tag{1.76a}$$

Equation (1.76a) can be integrated by parts to give

$$S - S_o = RT\left(\frac{\partial\, ln\, Q}{\partial T}\right)_v - \int_o^T RT^2\left(\frac{\partial\, ln\, Q}{\partial T}\right)_v\left(-\frac{1}{T^2}\right) dT$$

$$= \frac{E - E_o}{T} + R\, ln\, \frac{Q}{Q_o} \qquad (1.76b)$$

where Q_o is the partition function at zero temperature or, in other words, the ground state degeneracy g_o. The constant of integration S_o is determined by a comparison between equation (1.76b) and the relation

$$S = R\, ln\, \frac{Q}{N} + \frac{E - E_o}{T} + R \qquad (1.77)$$

which is equivalent to equation (1.49) except that finite zero state energy E_o is included. By inspection, one sees that S_o must be

$$S_o = R\, ln\, \frac{Q_o}{N} + R \qquad (1.78)$$

and the entropy per mol may finally be expressed as

$$S = RT\left(\frac{\partial\, ln\, Q}{\partial T}\right)_v + R\, ln\, \frac{Q}{N} + R \qquad (1.79)$$

Note that it makes no difference whether Q or Q/N is used in the logarithmic derivatives, but the ratio Q/N must appear in the second term of equation (1.79) when gas phase is considered. Often the symbol Q alone is understood to signify the ratio Q/N for the gas phase, but the notation that shows explicit dependence on N is retained here to call attention to this later when discussing chemical equilibrium.

At this point, one might ask whether entropy satisfies the definition of an extensive property (i.e., the sum of entropy of the parts of a system equals the total) in view of the fact that S appears to vary as a nonlinear function of N, namely, $-ln\, N$, according to equation (1.79). However, in chapter 3, the kinetic energy partition function for free particles is found to be proportional to volume V. Thus, so long as the ratio V/N remains constant, the entropies of the parts of a system are additive as required. If, however, the volume is allowed to change, such as when a partition is removed between two masses of different gas, the zero point entropy of each gas is changed by the increase in volume and the resulting change in entropy is known as the entropy of mixing.

The free energy F is defined as

$$F - E_o = (E - E_o) - TS = -RT\, ln\, \frac{Q}{N} - RT \qquad (1.80)$$

and, according to equation (1.9), the pressure is

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = RT\left(\frac{\partial\ ln\ Q}{\partial V}\right)_T \tag{1.81}$$

For the ideal or dilute gas, the particles behave essentially as free particles, in which case Q is proportional to V (see eq. (1.59)), so that

$$\left(\frac{\partial\ ln\ Q}{\partial V}\right)_T = \frac{1}{V} \quad \text{(ideal gas)} \tag{1.82}$$

$$p = \frac{RT}{V} \quad \text{(ideal gas)} \tag{1.83}$$

The remaining thermodynamic properties can be expressed in terms of those given above. Thus, all thermodynamic quantities can be derived from the partition function Q, which, in turn, is a function of the independent variables T and V.

Problem 1.4: Show that, if Q is proportional to V (i.e., the gas is ideal),

$$\left(\frac{\partial\ ln\ Q}{\partial T}\right)_p = \left(\frac{\partial\ ln\ Q}{\partial T}\right)_v + \frac{1}{T} \tag{1.84}$$

Show that the enthalpy is

$$H - E_O = RT^2\left(\frac{\partial\ ln\ Q}{\partial T}\right)_p \tag{1.85}$$

Also show that the entropy of a gas may be expressed as

$$S = RT\left(\frac{\partial\ ln\ Q}{\partial T}\right)_p + R\ ln\ \frac{Q}{N} \tag{1.86}$$

and that the free enthalpy is

$$G - E_O = -RT\ ln\ \frac{Q}{N} \tag{1.87}$$

1.12 GIBBS' DEFINITION OF ENTROPY

The Boltzmann definitions of entropy considered previously (eqs. (1.22a) through (d)) are special cases of a yet more fundamental definition provided by Gibbs:

$$S = -k\sum_j p_j\ ln\ p_j \tag{1.22e}$$

where p_j is the probability that the system is in the state j and the summation extends over all possible states. This definition is most often used in information theory (e.g., when the concern is about how much information can be abstracted from the system rather than how much work). Entropy becomes a measure of the information content that cannot be abstracted given a certain level of noise (i.e., temperature). Incidentally, comparisons between information theory and thermodynamics immediately suggest the equivalence between information and work. Our present concern, however, is to show the equivalence between equation (1.22e) and the Boltzmann definition of entropy.

Consider first a system constrained to a given distribution function for the set of occupation numbers n_i. The W equivalent states of this system are assumed to be equally probable, thus $p_j = W^{-1}$ and, for such a system,

$$S = -k\sum_{j=1}^{W} \frac{1}{W}\, ln\, \frac{1}{W} = k\, ln\, W \tag{1.22b}$$

which is the relation used in section 1.5.

In a real system, we do not know the occupation numbers n_i exactly because these values fluctuate because of collisions or other processes; this lack of precise knowledge means that the entropy of the system is increased so far as we are concerned. However, if we know the occupation numbers very closely, as for systems at equilibrium or when we are following in close detail a chemical relaxation process for example, then we can assign the entropy rather precisely with equation (1.22b). To be more precise, we know only that the system maintains constant energy, and we assume that in equilibrium all sets of occupation numbers n_i that conserve this total energy are equally probable. Then $p_k = \Omega^{-1}$ and the equilibrium entropy of real systems is

$$S = -k \sum_{j=1}^{\Omega} \frac{1}{\Omega}\, ln\, \frac{1}{\Omega} = k\, ln\, \Omega \tag{1.22c}$$

The increase in entropy $k\, ln\, \Omega/W_{max}$ over the approximate equilibrium entropy $k\, ln\, W_{max}$ is a measure of the uncertainty introduced by fluctuations. The difference between equation (1.22c) and (1.22b) is somewhat academic since Ω is usually equated to W_{max} in numerical evaluation.

Still another definition of entropy is occasionally encountered in the literature. A system of n identical particles may be considered as a collection of n subsystems, each with an identical entropy $-k\sum_{k} p_k\, ln\, p_k$, where the summation now extends over all energy states available to the individual particles. The entropy of the system is then the sum of all n parts of the system:

$$S_{solid} = -nk \sum_{k} p_k\, ln\, p_k \tag{1.22f}$$

Equation (1.22f) is the entropy for a system of distinguishable particles such as in the solid phase where the particles are localized. For the gas phase, a factor $(-ln\, n!)$ is added to account for the fact that $n!$ of the different states for distinguishable particles corresponds to just one state of the indistinguishable, quantized gas particles:

$$S_{gas} = -nk \sum_k p_k \, ln \, p_k - ln \, n! \qquad (1.22g)$$

Now, given the distribution function n_i for particles in energy levels ε_i, which may have degeneracy g_i, the probability p_k can be expressed as

$$p_k = \frac{n_i}{ng_i} \qquad (1.88)$$

Equation (1.88) makes use of the assumption that the occupation numbers in degenerate states of the same energy are equal, a relation known to be valid for the equilibrium state at least. Then

$$S = k \sum_k \frac{n_i}{g_i} \, ln \, \frac{ng_i}{n_i} - k(n \, ln \, n - n) \qquad (1.89)$$

The summation may be performed over the degenerate states to give a summation over all levels i:

$$S = k \sum_i n_i \left(ln \, n + ln \, \frac{g_i}{n_i} \right) - k(n \, ln \, n - n)$$

$$= k \sum_i n_i \, ln \, \frac{g_i}{n_i} + nk \qquad (1.90)$$

Substituting the value of $ln \, W$ derived from equation (1.45) with Stirling's approximation

$$ln \, W = \sum_i n_i \, ln \, \frac{g_i}{n_i} + n \qquad (1.91)$$

one obtains

$$S = k \, ln \, W \qquad (1.22b)$$

which is the same relation defined in section 1.5. Thus we see that the Gibbs formulation of entropy is completely equivalent to the Boltzmann formulations used previously.

Let us now investigate the order of magnitude of the fluctuation correction term $k \, ln(\Omega/W_{max})$ in equation (1.22d). Let n_i be the number of particles in each energy level i of a gas at equilibrium (hence, $W = W_{max}$):

$$W_{max} = \prod_i \frac{g_i^{n_i}}{n_i!} \qquad (1.92)$$

In a small fluctuation from equilibrium, let δ_i be the number of particles shifted from level i to adjacent levels, which we assume will have nearly the same degeneracy g_i and nearly the same occupation number n_i, both of which are very large numbers. The δ_i values may be either positive or negative integers and the sum of all δ_i vanishes. The ratio of W, the fluctuating value of the thermodynamic probability, to W_{max} can then be expressed as

$$\frac{W}{W_{max}} = \prod_i g_i^{\delta_i} \frac{n_i!}{(n_i + \delta_i)!} \tag{1.93}$$

The logarithm of this ratio is, with Stirling's approximation,

$$\begin{aligned} ln \frac{W}{W_{max}} &= \sum_i \left[\delta_i \; ln \; g_i + ln \frac{n_i!}{(n_i + \delta_i)!}\right] \\ &= \sum_i [\delta_i \; ln \; g_i + n_i \; ln \; n_i - (n_i + \delta_i) ln(n_i + \delta_i)] \end{aligned} \tag{1.94}$$

Expand the logarithms and assume that very few of the numbers in each level are shifted ($\delta_i << n_i$):

$$(n_i + \delta_i) ln(n_i + \delta_i) = n_i \; ln \; n_i + \delta_i \; ln \; n_i + \delta_i + \frac{n_i}{2}\left(\frac{\delta_i}{n_i}\right)^2 - \frac{n_i}{6}\left(\frac{\delta_i}{n_i}\right)^3 + O\left[n_i\left(\frac{\delta_i}{n_i}\right)^4\right] \tag{1.95}$$

$$ln \frac{W}{W_{max}} \approx \sum_i \left[\delta_i \; ln \; g_i - \delta_i \; ln \; n_i - \frac{n_i}{2}\left(\frac{\delta_i}{n_i}\right)^2 + \frac{n_i}{6}\left(\frac{\delta_i}{n_i}\right)^3 + \ldots\right] \tag{1.96}$$

Now since the g_i and n_i terms are assumed to be nearly equal between the adjacent levels where exchanges occur and the sum of all δ_i vanishes, the first two terms of the summation in equation (1.96) are of small order. The largest term is the quadratic term in $(\delta_i/n_i)^2$

$$ln \frac{W}{W_{max}} \approx -\sum_i \frac{\delta_i^2}{2n_i}, \qquad \frac{W}{W_{max}} \approx e^{-\sum_i \delta_i^2/2n_i} \tag{1.97}$$

The possible number of states with changes δ_i in cell i are designated by Ω_i

$$\begin{aligned} \Omega_i &= \int W \, d\delta_i = W_{max} \, e^{-\sum_{j \neq i} \delta_j^2/2n_j} \int_{-\infty}^{\infty} e^{-\delta^2/2n} \, d\delta \\ &= W_{max} \, e^{-\sum_{j \neq i} \delta_j^2/2n_j} \sqrt{2n_i\pi} \end{aligned} \tag{1.98}$$

Now let all δ_i terms take all possible values independently of one another. (This actually overestimates the total number of possible states since the δ_i are restricted by the fact that the sum of all δ_i must vanish.)

$$\Omega = \sum_{\delta_j} \Omega_i = \int \ldots \int W \, d\delta_i \, d\delta_j \ldots = W_{max} \prod_i (2\pi n_i)^{1/2} \tag{1.99}$$

$$\ln \frac{\Omega}{W_{max}} = \sum_i \frac{1}{2} \ln (2\pi n_i) \tag{1.100}$$

This sum is exactly the negative of a sum that was neglected in using Stirling's approximation for the $\sum_i \ln n_i!$ (see eq. (1.47)). Since the estimate of $\ln \Omega / W_{max}$ found above is an upper limit, the approximation $\ln \Omega \doteq \ln W_{max}$ is indeed valid when the numbers n_i, which contribute appreciably to the total thermodynamic probability W, are all very large.

Problem 1.5: Show that, if a pure uniform gas is divided into several parts with the same number density, N_i/V_i, the sum of the entropy of the parts equals the entropy of the whole: $\Sigma\, S_i = S$.

Problem 1.6: Show that, if a collection of gases are mixed with mol fractions x_i, the entropy for 1 *mol* of the mixture is

$$S = \sum_i x_i S_i - R \sum_i x_i \ln x_i$$

where S_i is the *entropy per mole* of species i. The positive term $(-\sum_i x_i \ln x_i)$ is often called the entropy of mixing. However, it merely represents a correction to the zero point molar entropies to account for the fact that a mole of pure species i would, at the same density as the gas species i, occupy a larger volume than a molar volume of the gas mixture.

1.13 QUANTUM STATISTICS

In the statistics of particles considered thus far, each degenerate state available to the particles was treated as a distinguishable state. The particles themselves were considered distinguishable in solid phase where they are fixed at a definite location, and indistinguishable in gas phase where they are free to occupy any position. In either case, the model led to a Maxwell-Boltzmann distribution as the most probable; only the entropy decreased by a constant term $-nk(\ln n - 1)$ when the particles were indistinguishable.

In quantum statistics, the g_i degenerate states of energy cell i are treated as a cyclic array of indistinguishable states and a cyclic array of g_i objects has $(g_i - 1)!$ permutations. This corresponds to the different ways of indexing the degenerate states. (Note the difference between permutations of cyclical and linear arrays - a linear array of g_i objects has $g_i!$ permutations.)

In addition, two classes of quantum particles exist - fermions and bosons. These particles are described by wave functions developed later in chapter 3 and thereafter. Fermions are particles composed of an odd number of fundamental particles, each having a half-integer unit of angular momentum. (For purposes of this book, we consider only the following fundamental particles: protons, neutrons, and electrons.) A collection of fermions is found to require an asymmetric wave function, with the consequence that two fermions *cannot* occupy the same state. Bosons, on the other hand, are particles composed of an even number of fundamental particles, and a collection of bosons is required to have a symmetric wave function, with the consequence that two or more bosons *can* occupy the same state. These consequences follow from the Pauli exclusion principle and are discussed in more detail in chapter 4 in connection with nuclear spin effects in rotating molecules. For the present, we are concerned with the statistics obeyed by these two classes of particles.

Fermions are restricted to one particle per state with g_i states in each energy cell. The number of ways n_i indistinguishable particles can be arranged in g_i states is $g_i!/n_i!(g_i - n_i)!$. Note that $g_i > n_i$. Thus the total thermodynamic probability is (see appendix 1-A for a derivation)

$$W = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!} \tag{1.101}$$

Now take the logarithm of equation (1.101), add equations (1.31) and (1.32) with Lagrange multipliers α and β, respectively, and maximize the result by setting the derivative with respect to n_i equal to zero as before. In this case, the numbers g_i and $(g - n_i)!$ can often be small and the use of Stirling's approximation is difficult to justify; nevertheless, the same results are obtained once again as with the more rigorous Darwin-Fowler method. The Fermi-Dirac distribution function for fermions is found to be

$$n_i = \frac{g_i}{e^{\alpha+\beta\epsilon_i} + 1} \tag{1.102}$$

the same form obtained for the Maxwell-Boltzmann distribution except for the term (+1) added to the exponential function in the denominator.

Any number of bosons can occupy each state and, in this case, the $(g_i - 1)!$ cyclical permutations of the states are indistinguishable as well. This cyclical permutation is equivalent to a linear permutation of $(g_i - 1)$ partitions between states. The total number of ways to permute $(n_i + g_i - 1)$ objects in a linear array, when n_i belong to one class of indistinguishable objects and $g_i - 1$ to another class of indistinguishable objects, is $(n_i + g_i - 1)!/n_i!(g_i - 1)!$. Thus, in this case, the thermodynamic probability is (again see appendix 1-A)

$$W = \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \tag{1.103}$$

Once again, maximizing the sum of $\ln W$ and equations (1.31) and (1.32) with Lagrange multipliers α and β, one obtains for the Bose-Einstein distribution of bosons,

$$n_i = \frac{g_i}{e^{\alpha+\beta\varepsilon_i} - 1} \tag{1.104}$$

the same form obtained for the Maxwell-Boltzmann distribution except for the term (-1) added to the exponential function in the denominator.

Problem 1.7: Show that if $ln\ x!$ is assumed to be equal to $(x\ ln\ x - x)$, without restriction, the thermodynamic probabilities of equations (1.101) and (1.103) lead to the most probable distribution functions (1.102) and (1.104), respectively.

One can see that, so long as the factor $e^{\alpha+\beta\varepsilon_i}$ is large compared with unity, the Fermi-Dirac and Bose-Einstein distributions, equations (1.102) and (1.104), respectively, are practically identical with the Maxwell-Boltzmann distribution, equation (1.34). This is indeed the case wherever normal gas temperatures and densities obtain; the differences between these distributions become apparent only at exceedingly high densities and/or low temperatures (as shown in ch. 3). One might consider the factors $g_i^{n_i}/n_i!$ in equation (1.45) as expresions for the number of ways n_i classical gas particles can be assigned to g_i states within a unit band of energy. This number is not necessarily an integer, but it is bracketed by the comparable integer expressions for the fermion and boson distributions:

$$\frac{g_i!}{n_i!(g_i - n_i)!} > \frac{g_i^{n_i}}{n_i!} > \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \tag{1.105}$$

provided $g_i > n_i$. At normal temperatures and densities, $g_i >> n_i$, and, in this case, all these expressions are approximately equal.

1.14 CONCLUDING REMARKS

Statistical mechanics has made three very significant additions to thermodynamics. First, it permits all thermodynamic quantities to be evaluated from spectroscopic energy level data, which are so precise that the thermodynamic quantities can be determined accurately whenever spectroscopic data are available. Second, statistical mechanics establishes the absolute level of entropy and therefore the level of the free energies relative to the zero point energy. Finally, entropy is interpreted as a measure of the probability that the system may be found in the given state. Then, if one accepts the fundamental postulate of statistical mechanics that all spontaneous processes lead toward a more probable state of the system, the reason entropy increases spontaneously and becomes a maximum at equilibrium becomes apparent.

APPENDIX 1-A: DERIVATIONS OF THERMODYNAMIC PROBABILITIES

Statistical mechanics is based on mathematical expressions for permutations and combinations of objects. Those expressions used in the derivations of statistical distribution functions are reviewed briefly.

Consider first the number of ways to arrange distinguishable particles in order. The first particle can be chosen from any of the n particles, the second from the $(n - 1)$ remaining, the third from the $(n - 2)$ remaining, and so on until the *nth* position is filled with the remaining particle. Thus, the number of different ways to arrange n distinguishable particles in order is

$$W = n(n - 1)(n - 2) \cdots 3 \cdot 2 \cdot 1 = n! \tag{1-A1}$$

If these n particles are now put into a single level where they are indistinguishable, all $n!$ of these permutations are the same so far as any observable of the system is concerned, and the number of different states of the system reduces to

$$W = \frac{n!}{n!} = 1$$

In the systems of interest, the particles do not all reside in the same level, but n_1 particles are in level 1, n_2 in level 2, . . ., n_i in level i, and so on. So far as an observable of the system is concerned, the $n_i!$ possible permutations of the particles in level i all yield the same result, so the number of equivalent states of the total system (defined in section 1.6 as the thermodynamic probability) is

$$W = \frac{n!}{\prod_k n_k!} \tag{1-A2}$$

A crystal lattice is a system for which each particle of the system is distinguishable by virtue of its position in the lattice. The above expression can be used for the thermodynamic probability of such a system if each energy state is counted separately, even though some of the states may be degenerate, that is, have the same energy level. In practice, for convenience of computation, the states with the same energy ε_i are usually grouped together and the occupation number n_i refers to the total number of particles in all g_i states with identical energy. If there is no restriction on the number of particles that can occupy each state, the first particle of the group n_i can be assigned in g_i ways, the first two can be assigned in g_i^2 ways, the first three in g_i^3 ways, and so on, until all n_i particles have g_i^{ni} separate ways in which they can be assigned. The expression for the thermodynamic probability then becomes

$$W = n! \prod_i \frac{g_i^{n_i}}{n_i!} \tag{1-A3}$$

the relation used in the text to obtain the solid phase distribution law and entropy.

For the gas phase, the particles are free to exchange positions to a good approximation and the $n!$ permutations of all possible exchanges are deemed to result in the same observable state of the total system. Thus, for the gas phase, the thermodynamic probability is taken to be

$$W = \prod_i \frac{g_i^{n_i}}{n_i!} \tag{1-A4}$$

The models above describe systems for which the particles are distinguishable in principle, but subsequently allow exchanges of particles in position or energy state so that the observable state of the total system is unchanged. These models adequately describe systems of particles that have essentially a continuous spectrum of energy and position and a particle density small compared with its density of degenerate states - in other words, a system of classical particles.

At low temperatues or high densities, the quantum nature of the particles must be considered, in which case the statistics of fundamentally indistinguishable particles must be treated more rigorously. Quantum particles are of two types, fermions and bosons. Consider first a system of fermions. Of the g_i states available with the same energy ε_i, n_i of these are occupied with a single particle each and the $(g_i - n_i)$ remaining are empty. The empty states are considered indistinguishable and the filled states are also considered indistinguishable, but the filled states are considered distinguishable from the unfilled states since the particles and states are different *things*. Of the $g_i!$ different ways to permute the total number of states, the $n_i!$ different ways to permute the filled states and the $(g_i - n_i)!$ different ways to permute the unfilled states are considered to result in the same observable or equivalent state of the total system. Thus the number of ways n_i indistinguishable particles can be assigned to g_i states of equal energy with no more than one particle per state is

$$W_i = \frac{g_i!}{n_i!(g_i - n_i)!}$$

Then the total number of equivalent ways all n fermions can be assigned the occupation numbers n_i is the product of all W_i:

$$W = \prod_i W_i = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!} \tag{1-A5}$$

the thermodynamic probability used for a gas system of fermions.

For a gas system of bosons, any number of particles can occupy any one of the degenerate energy states. The total number of ways n_i objects can be divided by $g_i - 1$ partitions (which group the objects into g_i different states) is the total number of permutations of n_i and $g_i - 1$ *things*, taken together, that is, $(n_i + g_i - 1)!$. But the $n_i!$ rearrangements of the indistinguishable particles and the $(g_i - 1)!$ rearrangements of the partitions all lead to the same observable state, so the number of different assignments available to the n_i particles in the g_i states, with no restriction on the number of particles per state, is

$$W_i = \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}$$

The total number of equivalent ways all n bosons can be assigned the occupation numbers n_i is again the product of all W_i:

$$W = \prod_i W_i = \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \tag{1-A6}$$

the thermodynamic probability used for a gaseous system of bosons.

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CHAPTER 2 - CHEMICAL EQUILIBRIUM

2.1 SUMMARY

The entropy of a gas system with the number of particles subject to external control is maximized to derive relations between the thermodynamic variables that obtain at equilibrium. These relations are described in terms of the chemical potential, defined as equivalent partial derivatives of entropy, energy, enthalpy, free energy, or free enthalpy. At equilibrium, the change in total chemical potential must vanish. This fact is used to derive the equilibrium constants for chemical reactions in terms of the partition functions of the species involved in the reaction. Thus the equilibrium constants can be determined accurately, just as other thermodynamic properties, from a knowledge of the energy levels and degeneracies for the gas species involved. These equilibrium constants permit one to calculate the equilibrium concentrations or partial pressures of chemically reacting species that occur in gas mixtures at any given condition of pressure and temperature or volume and temperature.

2.2 INTRODUCTION

According to the fundamental postulate of Statistical Mechanics formulated in chapter 1, the equilibrium state of a system is the most probable one consistent with the constraints imposed on the system. Since entropy increases with probability, the equilibrium state is alternatively described as that state to which spontaneous processes lead, resulting in a maximum in entropy. The word spontaneous is somewhat ambiguous in this statement; usually, it means that the irreversible process leading from a nonequilibrium state to the equilibrium state is allowed to proceed undisturbed in a system kept at constant energy and volume or at constant enthalpy and pressure. One should not infer that all irreversible processes leading to equilibrium must increase entropy; it is perfectly feasible to devise such a process in which the entropy of the internal system is decreased merely by subtracting heat or work from the system, for example.

Generally, as a closed system (i.e., a system with zero mass addition or subtraction) approaches the equilibrium state by some arbitrary irreversible path (which may include heat addition or subtraction), a typical inequality that obtains, according to the results in chapter 1, is

$$dE + p\,dV - T\,dS < 0 \tag{2.1a}$$

One can see immediately that if the system is constrained to constant E and constant V (i.e., the system is isolated from its surroundings), then the incremental changes of entropy dS that occur in the system during the irreversible process are always greater than zero since T is a positive quantity. Thus, if E and V are kept constant, the entropy is maximized as the system irreversibly approaches equilibrium. Similarly, if S and V are kept constant, the increments in energy dE are always negative, and the energy is then minimized at equilibrium.

To illustrate how entropy of a closed system can also decrease in an irreversible process leading to equilibrium, we can relax the requirement that energy be kept constant, but keep the volume constant as before. Figure 2.1 depicts the path of several such processes with paths along a constant volume plane in energy, entropy, and volume space. One equilibrium condition is represented by the point O in this plane; the locus of all equilibrium points at constant volume forms the equilibrium state line $O'O''$ in the constant volume E,S plane; this line is the intersection of the E,S plane with the equilibrium surface, defined by the equilibrium function $E(S,V)$ in three-dimensional E,S, and V space.

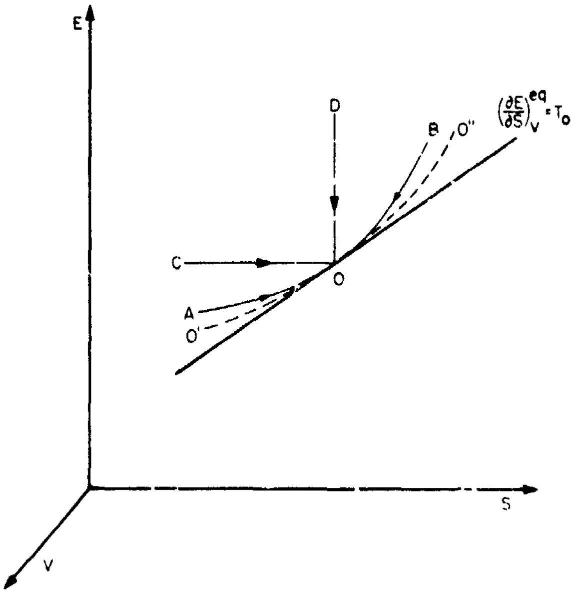

Figure 2.1.- Relations between energy E and entropy S in irreversible approaches to equilibrium point O at constant volume V.

Away from the equilibrium surface, at least three variables are required to define the state of the system; only three are required if only one degree of freedom of the system is out of equilibrium and one additional variable is required for each additional degree of freedom out of equilibrium. However, in an *infinitesimal region* next to the equilibrium surface, the state of the system can be defined by only two independent variables. In the present case, volume and entropy are chosen as the independent variables and the systems are constrained to a fixed volume. (A fixed volume is a simple constraint to impose experimentally, of course, though this is not essential to the argument.) Thus, in a region very near the equilibrium line along a constant volume path,

$$E = E(S,V) \; , \qquad dE = \left(\frac{\partial E}{\partial S}\right)_V dS \; , \qquad \left(\frac{\partial E}{\partial S}\right)_V^{eq} = T \qquad (2.1b)$$

For an arbitrary nonequilibrium path approaching the equilibrium region at the point O (fig. 2.1),

$$dE - T_0 \, dS < 0 \qquad (2.1c)$$

where T_O is the equilibrium temperature at point O. Thus, if the path approaches point O from lower values of entropy (path AO), the slope of the path must be less than T_O, whereas if the path approaches point O from higher values of entropy (path BO), the slope of the path must be greater than T_O. This means that the part of the E,S plane below and to the right of the constant slope line $(\partial E/\partial S)_V = T_O$ through the point O is inaccessible to the system. The equilibrium state at point O can be approached only from the region above and to the left of this line. If both E and V are kept constant, the process approaches equilibrium along line CC and the entropy is maximized at equilibrium. If S and V are kept constant, the process approaches equilibrium along line DO and the energy is minimized at equilibrium. These nonequilibrium process paths are *irreversible paths*.

The same situation holds at any point along the equilibrium line, of course. The slope of any arbitrary irreversible process path approaching the equilibrium line is related to the slope of that line at the point of approach by the inequality

$$\left[\left(\frac{\partial E}{\partial S}\right)_V^{noneq} - \left(\frac{\partial E}{\partial S}\right)_V^{eq}\right] dS < 0 \tag{2.1d}$$

As the equilibrium line is approached from a lower value of entropy ($dS > 0$), the slope of the path an infinitesimal distance away from the equilibrium point must be less than the slope of the equilibrium line at that point:

$$\left(\frac{\partial E}{\partial S}\right)_V^{noneq} \underset{dS>0}{<} \left(\frac{\partial E}{\partial S}\right)_V^{eq} \tag{2.2a}$$

On the other hand, if the equilibrium point is approached from a higher value of entropy ($dS < 0$), the reverse inequality holds:

$$\left(\frac{\partial E}{\partial S}\right)_V^{noneq} \underset{dS<0}{>} \left(\frac{\partial E}{\partial S}\right)_V^{eq} \tag{2.2b}$$

In other words, the curvature $(\partial^2 E/\partial S^2)_V^{noneq}$ for any irreversible constant volume process path near an equilibrium point must be positive:

$$\left(\frac{\partial^2 E}{\partial S^2}\right)_V^{noneq} = \lim_{\Delta S\to 0} \frac{1}{\Delta S}\left[\left(\frac{\partial E}{\partial S}\right)_V^{eq} - \left(\frac{\partial E}{\partial S}\right)_V\right] > 0 \tag{2.2c}$$

In problem 2.1, the reader is asked to deduce that the curvature of the equilibrium line $(\partial^2 E/\partial S^2)_V^{eq}$ is also positive.

Problem 2.1: Consider a nonequilibrium state described by three variables, namely, V, S, and T. Note that S and T are defined by a nonequilibrium distribution function as in chapter 1. For a segment of the process path not at the equilibrium point, the energy is expressed as

$$E = E(V, S, T) \tag{2.3a}$$

Expand the first derivatives of E for the nonequilibrium path about the closest equilibrium point and show that, at equilibrium,

$$\left(\frac{\partial E}{\partial T}\right)^{eq}_{S,V} = 0 \tag{2.3b}$$

$$\left(\frac{\partial^2 E}{\partial T^2}\right)^{eq}_{S,V} > 0 \tag{2.3c}$$

so that energy is minimized at equilibrium for any process path occurring at constant S and V.

The same type of reasoning can be applied using other sets of thermodynamic variables to show that entropy is maximized by any process occurring at constant H and p, for example, or that enthalpy is minimized by any process occurring at constant S and p. The most useful relations of this type involve the free energies. The Helmholtz free energy F is minimized at equilibrium for systems maintained at constant T and V, and the Gibbs free energy G is minimized at equilibrium for systems maintained at constant T and p (as the reader is asked to show in problem 2.2).

Problem 2.2: Show that the Helmholtz free energy F is minimized by an irreversible process occurring at constant V and T, which leads to equilibrium, and that T is minimized by an irreversible process occurring at constant F and V, which leads to equilibrium. Show that the curvature $(\partial^2 F/\partial T^2)_V$ for any process path in a constant volume F, T plane is positive at the equilibrium point. Sketch a curve of irreversible process paths on the F, T plane about the equilibrium point and show the region of this plane which is inaccessible to real systems. Deduce similar relations for the Gibbs free energy.

2.3 THERMODYNAMIC RELATIONS IN OPEN-SYSTEM GAS MIXTURES

In the previous chapter, closed systems composed of a single pure gas with constant number of particles were considered. Now, a system composed of a mixture of gases is treated and, for the moment, the number of particles is left open to external control. Then the thermodynamic properties all become functions of the number n_i of each species involved, as well as of two other independent thermodynamic variables. Let the entropy take the form

$$S = S(E,V,n_1,n_2,\ .\ .\ .) \tag{2.4}$$

Then the differential of entropy is

$$dS = \left(\frac{\partial S}{\partial E}\right)_{V,n_i} dE + \left(\frac{\partial S}{\partial V}\right)_{E,n_i} dV + \sum_i \left(\frac{\partial S}{\partial n_i}\right)_{E,V,n_j} dn_i \tag{2.5}$$

The two partial derivatives of entropy with fixed numbers n_i are the same as though the system were closed, with a fixed number of particles. Then, according to the results found in the last chapter for such systems, equations (1.9) and (1.11),

$$\left(\frac{\partial S}{\partial V}\right)_{E,n_i} = \frac{p}{T} \tag{2.6}$$

$$\left(\frac{\partial S}{\partial E}\right)_{V,n_i} = \frac{1}{T} \tag{2.7}$$

A quantity $\overline{\mu_i}$, the chemical potential per molecule, is defined as

$$\overline{\mu_i} = -T\left(\frac{\partial S}{\partial n_i}\right)_{E,V,n_{j\neq i}} \tag{2.8}$$

where all n_j except n_i are maintained constant. The chemical potential $\overline{\mu_i}$ divided by the temperature is just the negative change in entropy created when one molecule of species i is added to the gas mixture at fixed energy and volume. The symbol μ is reserved for the total chemical potential per mol and μ_i designates the chemical potential per mol of species i, or $N\overline{\mu_i}$.

Equation (2.5) can now be expressed as

$$dS = \frac{dE}{T} + \frac{p\,dV}{T} - \frac{1}{T}\sum_i \overline{\mu_i}\,dn_i \tag{2.9}$$

If entropy is to be a maximum ($dS = 0$) in systems kept at constant E and V, the change in total chemical potential must vanish:

$$\Delta\mu = \sum_i \overline{\mu_i}\,dn_i = 0 \tag{2.10}$$

Equation (2.10) is very important because it is the *general condition for thermodynamic equilibrium*. This relation holds for both open and closed systems. Note that a closed system is merely a special type of open system for which every particle abstracted is re-introduced, perhaps as another species.

If energy is taken to be the dependent variable, equation (2.9) is conveniently rearranged in the form

$$dE = -p\,dV + T\,dS + \sum_i \overline{\mu_i}\,dn_i \tag{2.11}$$

But energy can also be considered a function of the variables V, S, and n_i,

$$E = E(V,S,n_1,n_2, \ldots) \tag{2.12}$$

so that the derivative of energy is

$$dE = \left(\frac{\partial E}{\partial V}\right)_{S,n_i} dV + \left(\frac{\partial E}{\partial S}\right)_{V,n_i} dS + \sum_i \left(\frac{\partial E}{\partial n_i}\right)_{S,V,n_j} dn_i \tag{2.13}$$

The partial derivatives with constant n_i are again the values for a closed system with a fixed number of particles found in equation (1.9) and (1.11):

$$\left(\frac{\partial E}{\partial V}\right)_{S,n_i} = -p \tag{2.14}$$

$$\left(\frac{\partial E}{\partial S}\right)_{V,n_i} = T \tag{2.15}$$

so that equation (2.13) becomes

$$dE = -p\ dV + T\ dS + \sum_i \left(\frac{\partial E}{\partial n_i}\right)_{S,V,n_j} dn_i \tag{2.16}$$

Now one can see by comparison of equation (2.16) with (2.11) that an alternative definition of the chemical potential per molecule is

$$\overline{\mu_i} = \left(\frac{\partial E}{\partial n_i}\right)_{S,V,n_j} \tag{2.17}$$

which is the change in energy created when just one molecule of species i is added to the gas mixture at fixed entropy and volume. The derivation of additional thermodynamic relations of interest is left to the reader as problem 2.3.

Problem 2.3: Show that for a mixture of gases in an open system.

$$dH = V\ dp + T\ dS + \sum_i \overline{\mu_i}\ dn_i \tag{2.18}$$

$$dF = -p\ dV - S\ dT + \sum_i \overline{\mu_i}\ dn_i \tag{2.19}$$

$$dG = V\ dp - S\ dT + \sum_i \overline{\mu_i}\ dn_i \tag{2.20}$$

and that the chemical potential $\overline{\mu_i}$ may be defined by any one of the partial derivatives:

$$\overline{\mu_i} = -T\left(\frac{\partial S}{\partial n_i}\right)_{E,V,n_j} = \left(\frac{\partial E}{\partial n_i}\right)_{S,V,n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_j} = \left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_j} = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} \tag{2.21}$$

Many authors make a point of classifying chemical potential as one of the intensive thermodynamic variables since $\overline{\mu_i}$ is a derivative of one extensive quantity with respect to another extensive quantity, which obviously depends only on the gas mixture involved and not on the total amount of mixture contained in the system. In this sense, all *specific* thermodynamic variables measured with respect to a unit quantity of gas, such as energy per molecule or energy per mol, are intensive properties. Like $\overline{\mu_i}$, they are derivatives or ratios of two extensive quantities. However, a *total chemical potential* can be defined for the system which is the sum of all chemical potentials of the parts of the system; this total chemical potential is an extensive quantity just as total energy, total enthalpy, total free energy, or total free enthalpy. This group of properties clearly belongs to a different class than the inherently intensive properties such as pressure, temperature, and density.

2.4 CLOSED-SYSTEM GAS MIXTURES WITH CHEMICAL REACTION

Now we return to the problem of a gas mixture in a *closed system*, that is, with no particles added or subtracted from the external environment, but where the numbers of the gas particles can change due to chemical reaction:

$$\sum_j a_j A_j = \sum_k b_k B_k \tag{2.22}$$

The reactant species are designated by A_j and the product species by B_k, and the corresponding stoichiometric coefficients of the reaction are a_j and b_k, respectively. These are the molecule numbers (or the mol numbers) which balance the equation.

The forward rate of reaction (2.22) can be expressed in terms of the partial pressures of the reactants and the forward rate coefficient k_f

$$R_f = k_f \prod_j (p_j)^{a_j} \tag{2.23}$$

and the reverse rate in terms of the partial pressures of the products and the reverse rate coefficient k_r

$$R_r = k_r \prod_k (p_k)^{b_k} \tag{2.24}$$

At equilibrium, these rates must be equal and the ratio of the forward and reverse rate coefficients at equilibrium is, by definition, the equilibrium constant K_p:

$$K_p = \frac{k_f}{k_r} = \frac{\prod_k (p_k)^{b_k}}{\prod_j (p_j)^{a_j}} \tag{2.25}$$

The equilibrium constant is really a function of temperature, but it is called a constant to focus attention on the concept that it is independent of pressure or any other thermodynamic variable except temperature, at least under ideal conditions. Historically, the term arose because rate experiments were conveniently made under constant temperature conditions.

The rates can also be expressed in terms of concentrations c, which may be expressed in molecules per unit volume n/v, or mols per unit volume $1/V$, or mass per unit volume M/V, for example. (Mols per unit volume are the units used here.) The equilibrium constant K_c is defined similar to the above:

$$K_c = \frac{\prod_k (c_k)^{b_k}}{\prod_j (c_j)^{a_j}} \tag{2.26}$$

For dilute or ideal gas species, $c = p/RT$ and the two equilibrium constants are then related by

$$K_p = (RT)^{\Delta n} K_c \tag{2.27}$$

where Δn is the change in the number of molecules of the system per molecular reaction:

$$\Delta n = \sum_k b_k - \sum_j a_j \tag{2.28}$$

The equilibrium constants K_p and K_c are now derived in terms of the partition functions of the chemical species involved in the reaction. At equilibrium, the change in total chemical potential must vanish. The changes in different species numbers dn_i are related by the chemical reaction (2.22) according to

$$\frac{dn_j}{a_j} = - \frac{dn_k}{b_k} = d\lambda \tag{2.29}$$

where $d\lambda$ is a common factor of proportionality. Thus equation (2.10) becomes

$$\Delta\mu = \sum_i \overline{\mu_i}\, dn_i = d\lambda \left(\sum_j a_j \overline{\mu_j} - \sum_k b_k \overline{\mu_k} \right) = 0 \tag{2.30}$$

or, in other words, the decrease in chemical potential caused by the disappearance of the reactant species must just balance the increase in chemical potential resulting from the appearance of product species:

$$\sum_j a_j \overline{\mu_j} = \sum_k b_k \overline{\mu_k} \tag{2.31}$$

The chemical potentials may be evaluated in principle from any one of the partial derivatives listed in equation (2.21). In practice, derivatives of the free energy or the free enthalpy are most convenient to evaluate. The free enthalpy for n particles may be expressed, using the definition of enthalpy and equation (1.77) for entropy, as

$$\begin{aligned} G &= H - TS \\ &= n\varepsilon_o + n(\varepsilon - \varepsilon_o) + pV - T\left[nk\, ln\, \frac{Q}{n} + n\left(\frac{\varepsilon - \varepsilon_o}{T}\right) + nk\right] \\ &= n\varepsilon_o + pV - nkT\left(1 + ln\, \frac{Q}{n}\right) \end{aligned} \tag{2.32}$$

where the total number of particles has been left as n, rather than the constant Avagadro number, N, to call attention to the fact that this is the variable of differentiation and, accordingly, V is taken as the total volume rather than the molar volume V. Then the chemical potential per molecule is

$$\bar{\mu} = \left(\frac{\partial G}{\partial n}\right)_{p,T} = \varepsilon_o + p\left(\frac{\partial V}{\partial n}\right)_p - kT\left(1 + \ln\frac{Q}{n}\right) - nkT\left[\left(\frac{\partial \ln Q}{\partial V}\right)_T\left(\frac{\partial V}{\partial n}\right)_p - \frac{1}{n}\right] \qquad (2.33)$$

Note that the ideal gas assumption has not been invoked here, so the results above are general. However, from equation (1.81),

$$\left(\frac{\partial \ln Q}{\partial V}\right)_T = \frac{p}{nkT} \qquad (2.34)$$

so that equation (2.33) becomes

$$\bar{\mu} = \varepsilon_o - kT \ln\frac{Q}{n} \qquad (2.35)$$

If free energy is chosen as the starting point, exactly the same results follow:

$$F = n\varepsilon_o - nkT\left(1 + \ln\frac{Q}{n}\right) \qquad (2.36)$$

$$\bar{\mu} = \left(\frac{\partial F}{\partial n}\right)_{V,T} = \varepsilon_o - kT\left(1 + \ln\frac{Q}{n}\right) - nkT\left(-\frac{1}{n}\right)$$

$$= \varepsilon_o - kT \ln\frac{Q}{n} \qquad (2.37)$$

Note that Q/n is the quantity that keeps appearing in the thermodynamic relations for gases. Often the tacit assumption is made that this is the quantity meant when one speaks of the partition function for gases. However, the ratio Q/n is defined here as the symbol $\bar{Q}$:

$$\bar{Q} = Q/n \qquad (2.38)$$

as a reminder that this quantity is the partition function of the species divided by the number of molecules of the species contained in the gas system. Normally, we consider one mol of particles at a time, for which $n = N$. Also, focusing attention on the chemical potential per molecule $\bar{\mu}$ emphasizes the idea that this potential is a derivative or, in other words, a ratio taken at the limit where the changes are vanishingly small. (The system is perturbed hardly at all by the addition of a single molecule.) However, in practice, one customarily works with the chemical potential per mole. Since the potential is clearly an additive quantity, this potential is simply

$$\mu = N\bar{\mu} = E_o - RT \ln \bar{Q} \qquad (2.39)$$

Whether μ or $\bar{\mu}$ is used in the equilibrium relations in equation (2.10) or (2.31) is immaterial in any case.

The partition functions may be expressed as functions of V and T or of p and T as desired. We now wish to relate Q to some arbitrary reference level or standard state where the volume is V_o. This is easy for the very dilute gas since Q is simply proportional to V (eq. (1.59)). Then

$$\ln Q = \ln Q_c + \ln \frac{V}{V_o} \tag{2.40}$$

where Q_c is the partition function at the standard state with molar volume equal to V_o. In terms of concentrations $c = 1/V$ (mols per unit volume) or similar units, equation (2.40) becomes

$$\ln Q = \ln Q_c - \ln \frac{c}{c_o} \tag{2.41}$$

where c_o is now a reference concentration that defines the standard state. Since the ideal gas law $pV = RT$ is obeyed for this case, equation (2.40) may also be expressed as

$$\ln Q = \ln Q_p - \ln \frac{p}{p_o} \tag{2.42}$$

and, in this case, p_o is a reference pressure that defines the standard state. The concept of a standard state is introduced because the standard state partition functions Q_c and Q_p can be treated as purely functions of temperature, and the variation of Q with concentration or pressure is accounted for in the separable term. For dilute or ideal gases, the concentration standardized partition function is

$$Q_c = \frac{Q}{V} = \frac{pQ}{RT} \tag{2.43}$$

while the pressure standardized partition function is

$$Q_p = pQ \tag{2.44}$$

Substituting the chemical potentials given by equation (2.39) into (2.31) yields the equilibrium condition

$$\frac{\Delta E_o}{RT} = \ln \frac{\prod_k \bar{Q}_k^{b_k}}{\prod_j \bar{Q}_j^{a_j}} \tag{2.45}$$

where ΔE is the change in zero point energy when the a_j mols of reactants form the b_k mols of products:

$$\Delta E_o = \sum_k b_k E_{o_k} - \sum_j a_j E_{o_j} \tag{2.46}$$

In other words, ΔE_o may be considered the heat of reaction extrapolated to zero temperature. In terms of the pressure standardized partition functions $\overline{Q}_p$ (see eq. (2.42)), equation (2.45) becomes

$$\frac{\Delta E_o}{RT} = ln \frac{\prod_k \overline{Q}_{p_k}^{b_k}}{\prod_j \overline{Q}_{p_j}^{a_j}} - ln \frac{\prod_k \left(\frac{p_k}{p_o}\right)^{b_k}}{\prod_j \left(\frac{p_j}{p_o}\right)^{a_j}} \tag{2.47}$$

Introducing the definition of the equilibrium constant K_p (eq. (2.25)) into the last term of equation (2.47) yields

$$ln \left(\frac{K_p}{p_o^{\Delta n}}\right) = - \frac{\Delta E_o}{RT} + ln \frac{\prod_k \overline{Q}_{p_k}^{b_k}}{\prod_j \overline{Q}_{p_j}^{a_j}} \tag{2.48}$$

Normally, the standard state pressure is taken as unity (e.g., 1 atm) so that equation (2.48) is often written without the dimensional term $p_o^{\Delta n}$. However, including it here reminds us that K_p is a dimensional quantity whenever Δn is different than zero.

Similarly, the equilibrium constant K_c can be related to the concentration standardized partition functions $\overline{Q}_c$. From equations (2.41) and (2.45),

$$\frac{\Delta E_o}{RT} = ln \frac{\prod_k \overline{Q}_{c_k}^{b_k}}{\prod_j \overline{Q}_{c_j}^{a_j}} - ln \frac{\prod_k \left(\frac{c_k}{c_o}\right)^{b_k}}{\prod_j \left(\frac{c_j}{c_o}\right)^{a_j}} \tag{2.49}$$

Again, introducing the definition of K_c (eq. (2.26)) into the last term of equation (2.49) yields

$$ln \left(\frac{K_c}{c_o^{\Delta n}}\right) = - \frac{\Delta E_o}{RT} + ln \frac{\prod_k \overline{Q}_{c_k}^{b_k}}{\prod_j \overline{Q}_{c_j}^{a_j}} \tag{2.50}$$

Once again, the standard condition c_o is normally taken as unity (e.g., 1 mol/liter) so that equation (2.50) is often written without the dimension term $c_o^{\Delta n}$.

Problem 2.4: Use equations (2.48) and (2.50) to verify the relation $K_p = (RT)^{\Delta n} K_c$.

We should mention that the equilibrium condition is often analyzed by equating the chemical potential to the free enthalpy. This is indeed true for ideal gases, the case treated here. From equations (2.32) and (2.39), one can see that for a molar quantity of gas ($n = N$),

$$\mu = G = E_O - RT \, ln \, \overline{Q} \tag{2.51}$$

Then the equilibrium condition requires that the summation ΔG should vanish

$$\Delta G = \sum_k b_k G_k - \sum_j a_j G_j = 0 \tag{2.52}$$

which leads to exactly the same results as above. However, equation (2.51) is satisfied only for the particular value of reference entropy given by equation (1.78) (in accord with the statistical definition of entropy $S = k \, ln \, W$), and, for another choice of zero point entropy, the sum ΔG will no longer vanish if the number of product molecules is different than the number of reactant molecules from which they are formed ($\Delta n \neq 0$) In fact, even with the zero point entropy given by equation (1.78), the Helmholtz free energy F cannot generally be used as a direct replacement for the chemical potential μ for constant volume processes. For a chemical reaction at constant volume and temperature, the sum

$$\Delta F = \sum_k b_k F_k - \sum a_j F_j \tag{2.53}$$

vanishes only if $\Delta n = 0$. These difficulties are avoided, however, when the chemical potential is treated as a derivative of G or F, as it should be. Then the results are independent of the zero point entropy.

Problem 2.5: Show that if the zero point entropy is shifted by a constant S^* different than zero, that is,

[illegible]

the chemical potential is still given by the same function of $\overline{Q}$,

[illegible]

Furthermore, show that the sum ΔG (eq. (2.52)) is then different than zero if Δn is different than zero, and that the sum ΔF (eq. (2.53)) vanishes for the same case only if [illegible]$^* = -F$.

2.5 CONCLUDING REMARKS

The curvature of the equilibrium surface in a three-coordinate thermodynamic variable space (such as energy, volume, and entropy) can be deduced from the first and second laws of thermodynamics. From this curvature, one can predict maximum and minimum relations that occur at equilibrium, such as the fact that entropy is maximized at equilibrium in any system kept at constant volume and energy, for example. An irreversible process need not always lead to an increase in entropy; indeed, spontaneous processes isolated from external influence do lead to an entropy maximum at equilibrium, but an irreversible path that decreases the entropy of a system can be arranged by suitable interaction with an external system. The only requirement is that the total entropy of both the system of interest and the external system must increase.

The equilibrium condition is given in terms of the chemical potential, which can be expressed in completely equivalent ways as partial derivatives of entropy, energy, enthalpy, free energy, or free enthalpy. Physically, the chemical potential per molecule represents quantities such as the increase in free energy when a single molecule is added to a system at fixed temperature and volume, or the increase in free enthalpy when a single molecule is added to a system at fixed temperature and pressure, for example.

At equilibrium, chemically reacting species exist in the proper ratio to balance the forward and reverse rates of reaction, which means that the change in chemical potential caused by the reaction vanishes. This relation has been used to express the chemical equilibrium constants (i.e., the ratio of the forward and reverse rate coefficients) in terms of the partition functions of the species involved, once again illustrating that any thermodynamic property of a system may be deduced from these partition functions. Sometimes the chemical potential is equated to the Gibbs free enthalpy in such derivations, which leads to the same result as when the chemical potential is taken to be the change in free enthalpy per molecule taken at constant pressure and temperature, because of the particular choice of zero entropy required in statistical mechanics. However, the concept that the free enthalpy is the chemical potential is basically misleading. The chemical potential is expressed equally well as the change in free energy per molecule taken at constant volume and temperature, but the chemical potential cannot be equated to free energy because the incorrect result is then obtained for chemical equilibrium whenever the reaction causes a change in the total number of molecules. Fundamentally, this situation occurs because the energy involved in the product of pressure and volume is not accounted for in free energy whereas it is a part of the free enthalpy. However, these conceptual difficulties are avoided when the chemical potential is merely treated as any one of the equivalent partial derivatives derived from the first and second law.

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CHAPTER 3 - QUANTUM PRINCIPLES AND FREE PARTICLES

3.1 SUMMARY

The quantum principles that establish the energy levels and degeneracies needed to evaluate the partition functions are explored. The uncertainty principle is associated with the dual wave-particle nature of the model used to describe quantized gas particles. The Schroedinger wave equation is presented as a generalization of Maxwell's wave equation; the former applies to all particles while the Maxwell equation applies to the special case of photon particles. The size of the quantum cell in phase space and the representation of momentum as a space derivative operator follow from the uncertainty principle. A consequence of this is that steady-state problems that are space-time dependent for the classical model become only space dependent for the quantum model and are often easier to solve. The partition function is derived for quantized free particles and, at normal conditions, the result is the same as that given by the classical phase integral The quantum corrections that occur at very low temperatures or high densities are derived. These corrections for the Einstein-Bose gas qualitatively describe the condensation effects that occur in liquid helium, but are unimportant for most practical purposes otherwise. However, the corrections for the Fermi-Dirac gas are important because they quantitatively describe the behavior of high-density conduction electron gases in metals and explain the zero point energy and low specific heat exhibited in this case.

3.2 INTRODUCTION

In the preceding two chapters, all the thermodynamic properties of gases, including the chemical equilibrium constants, were related to the partition functions. We now consider some of the quantum principles that establish the energy levels ε_i and the degeneracies g_i of atoms and molecules in gas phase - quantities needed to determine the partition functions. Strictly speaking, the energy levels are always quantized and the partition function is a sum over these levels. However, when the spacing between levels is small compared with kT, the classical phase integral will prove to be a useful approximation to the partition function since the integral is often easier to perform than the sum. The engineer who works on problems involving atomic and molecular properties needs some insight into quantum principles, primarily to give him the judgment to understand when classical methods can be used and when quantum methods must be invoked. The uncertainty principle of quantum mechanics is fundamental to this question.

3.3 UNCERTAINTY PRINCIPLE

The uncertainty principle can be related to the properties of the quantum mechanical wave functions (refs. 1 and 2) which describe the behavior of particles. These functions are just solutions to Schroedinger's equation, a famous equation often taken as the starting point or fundamental postulate (ref. 3) of quantum mechanics. However, we are apt to be staggered by the leap of intuition that would instantly postulate a complete second-order partial differential equation as the starting point for a description of the physical universe if we are not aware that Schroedinger discovered his equation by making some relatively simple modifications of the Hamilton-Jacobi equations that govern the motion of particles under the constraint of least action. Schroedinger's genius permitted him to realize that the time coordinate could profitably be treated as an imaginary variable; the Schroedinger equation was the result. Although this was the historical process of discovery, with hindsight, we can use a simple analogy to Maxwell's electromagnetic wave equations (ref. 4) that makes Schroedinger's result very plausible, particularly to engineers since they are so familiar with Maxwell's equations and their exceedingly successful applications in electrical engineering.

Experimentally, the fact has been repeatedly established (first by Davisson and Germer for electrons, e.g., see ref. 1) that moving particles possess the characteristics of waves. DeBroglie postulated that all particles behave something like photons (refs. 2 and 5) which are "wave particles" known to have a momentum p equal to their energy $h\nu$ divided by their velocity c:

$$p = \frac{h\nu}{c} = \frac{h}{\lambda} \tag{3.1}$$

where h is the Planck constant, ν is the frequency and λ is the wavelength. Furthermore, photons are known to obey Maxwell's equation

$$\nabla^2\Psi = \frac{1}{c^2}\frac{\partial^2\Psi}{\partial t^2} \tag{3.2}$$

where Ψ is the amplitude of the photon wave. By analogy, other particles can be expected to obey the same equation but with a different velocity of propagation, namely, $h\nu/p$ or $\nu\lambda$:

$$\nabla^2\psi = \frac{p^2}{h^2\nu^2}\frac{\partial^2\Psi}{\partial t^2} \tag{3.3}$$

A steady state, or standing wave, is formed when the space and time dependence are separable:

$$\Psi = \psi(x,y,z)e^{\pm i2\pi\nu t} \tag{3.4}$$

The product $\Psi\Psi^*$ is then independent of t, corresponding to the standing wave. The spatially dependent part of the wave function obeys the differential equation:

$$\nabla^2\psi = -\frac{4\pi^2 p^2}{h^2}\psi \tag{3.5}$$

The momentum squared, p^2, may be replaced with its equivalent $2m(E - U)$, where E is the total energy, U is the potential, and m is the particle mass. Then

$$\nabla^2\psi = -\frac{8\pi^2 m}{h^2}(E - U)\psi \tag{3.6}$$

which is the usual time-independent Schroedinger equation.

In Maxwell's equation, ψ^2 is interpreted as a factor proportional to the energy density of the wave (such as the square of the electric vector E^2 or of the magnetic vector H^2) (ref. 4), which is proportional to the photon density. In the Schroedinger equation, ψ^2 is interpreted as a probability (refs. 3 and 5), which is also proportional to particle density. For example, the probability that the particle will be in the volume element $d\tau$ is defined as

$$P = \frac{\psi\psi^*\,d\tau}{\int \psi\psi^*\,d\tau} \tag{3.7}$$

where $\int \psi\psi^*\,d\tau$ is a definite integral over all values of the coordinates involved and represents a normalization constant.

The uncertainty principle may be demonstrated from the wave function describing a free particle (i.e., a particle with constant momentum). If such a particle is moving in the x direction with momentum p_o, a solution to equation (3.5) is

$$\psi = C\,e^{ik_o x} \tag{3.8}$$

where the wave number k_o is $2\pi/\lambda_o$ or $2\pi p_o/h$. According to equation (3.4), the total time-dependent wave function may be expressed as

$$\Psi = C\,e^{ik_o(x-x_o)} \tag{3.9}$$

where x_o is $p_o t/m$. This function represents a plane wave traveling in the x direction with velocity p_o/m. However, it seems impossible to relinquish the idea that the object still retains some characteristics of a particle; that is, it should be localized in space. For example, if the probability is unity that the particle is somewhere in the interval Δx about x_c, then

$$\int_{x_o-\Delta x/2}^{x_o+\Delta x/2} \psi\psi^*\,dx = C^2\,\Delta x = 1 \tag{3.10}$$

Thus the amplitude must vanish ($C = 0$) if the particle is not localized ($\Delta x = \infty$). For Δx finite, a spectrum of wave numbers exists which is given by a Fourier analysis of the localized wave packet. The wave function may be expressed as the Fourier integral:

$$\psi(x) = \left(\frac{1}{2\pi}\right)^{1/2} \int_{-\infty}^{\infty} \phi(k) e^{ikx}\, dk \tag{3.11}$$

where the variable x now signifies the distance $(x - x_o)$ and $\phi(k)$ is the amplitude of the wave number spectrum:

$$\phi(k) = \left(\frac{1}{2\pi}\right)^{1/2} \int_{-\infty}^{\infty} \psi(x) e^{-ikx}\, dx \tag{3.12}$$

Thus, for the truncated wave packet,

$$\phi(k) = \left(\frac{1}{2\pi}\right)^{1/2} \int_{-\Delta x/2}^{\Delta x/2} \frac{e^{ix(k_o - k)}}{\sqrt{\Delta x}}\, dx = \left(\frac{2}{\pi\,\Delta x}\right)^{1/2} \frac{\sin(k_o - k)\Delta x/2}{k_o - k} \tag{3.13}$$

The intensity of the packet in the wave number interval dk about k is $\phi^2(k)$:

$$\phi^2(k)dk = \frac{2}{\pi\ \Delta x} \frac{\sin^2(k_o - k)(\Delta x/2)}{(k_o - k)^2}\, dk \tag{3.14}$$

If the effective width of the packet in k space is defined as the width of a square pulse Δk with the maximum height $\phi_m{}^2$ (i.e., $\Delta x/2\pi$) which has the same integrated intensity as given by equation (3.14), then

$$\frac{\Delta k\ \Delta x}{2\pi} = \int_{-\infty}^{\infty} \frac{2\ \sin^2(k_o - k)(\Delta x/2)}{\pi\ \Delta x(k - k_o)^2}\, dk = 1 \tag{3.15}$$

The wave number k is just $2\pi p/h$ and Δk is $2\pi\ \Delta p/h$. Thus,

$$\Delta p\ \Delta x = h \tag{3.16}$$

the familiar relation for the size of a quantized cell in momentum-position space, which was used in chapter 1 to make the classical phase integral dimensionless. Of course, the definition of the effective width of a nonrectangular pulse is somewhat arbitrary, but any reasonable definition leads to a relation similar to equation (3.16), where the product of the uncertainty in momentum and position is the order of Planck's constant. This is a general result for any wave packet having a smoothly varying pulse shape.

Problem 3.1: Show that the following normalized wave packet with a Gaussian envelope

$$\psi = C\ e^{-x^2/4\sigma^2}\ e^{ik_o x}$$

where σ is the standard deviation of the probability $\psi\psi^*$, leads to a Gaussian distribution in the intensity of the wave number spectrum. Furthermore, show that the same relation as equation (3.16) is obtained if the effective pulse widths are defined as $2\sqrt{\pi}$ times the standard deviations of the Gaussian distributions for ψ^2 and ϕ^2.

Our purpose here is not to refine the mathematical description of the uncertainty principle, but to emphasize that the principle comes about in a natural way as a consequence of trying to impose a dual nature on the "particle wave." One might consider discarding both the wave and particle model and attempt to construct an atomic theory that permits exact determination of all quantities appearing in it. Rice and Teller (ref. 6) point out that even though this might be possible in principle, since the mathematics of quantum mechanics is complete and free from contradictions, the theory would start from concepts having no immediate equivalent in everyday experience and one would run into all the difficulties in explaining the meaning of such an abstract theory that were avoided in formulating it. In addition, such a theory would doubtless fail to emphasize an important part of quantum mechanics known as the correspondence principle - that for certain limiting cases the laws of quantum theory converge on the laws of classical mechanics.

A distinction should be made between quantum transitions and classical processes. The quantum transition takes place between two different states with different physical properties. The classical process is associated with only one set of physical conditions and thus describes the situation when the change in physical properties between the initial and final states is negligibly small. Often this is the case in the limit of very high quantum numbers. In gases, the change in internal energy produced by collision must be small compared with the average energy per molecule, generally the order of kT, for classical methods to apply. The laws of quantum mechanics are a finished formalism, but the correspondence principle is useful in addition to its value as a limiting case because it helps to visualize and understand laws that are otherwise predominantly mathematical formalisms. Finally, Rice and Teller (ref. 6) conclude that any attempt to divorce quantum theory from the classical picture of particles and waves would destroy the significance of the correspondence principle and thus lead into a field where one is not allowed to use words that are used to express our everyday thinking and experience. They do not believe that a theory is possible which in its final analysis is not based on these words and therefore on classical physics and common sense. Bridgman (ref. 7) often expressed similar ideas.

One important consequence of the uncertainty principle is that a dynamic, steady-state process analyzed in terms of both space and time coordinates in classical mechanics can be transformed into a purely space-dependent problem in quantum mechanics. The latter is often easier to solve because the time parameter is missing since the time dependence is associated with the momentum coordinates of the system, which are represented in quantum mechanics by purely space-dependent derivative operators. To develop this relation (ref. 1), consider the Fourier integral representations of the wave function $\psi(x)$ and the wave number amplitude function $\phi(k)$ of a particle constrained to one-dimensional linear motion along the x coordinate, equations (3.11) and (3.12), respectively. The momentum of the particle is $\hbar k$ and the average value of momentum is given by

$$\overline{p_x} = \hbar \int_{-\infty}^{\infty} \phi^* k \phi \, dk \tag{3.17a}$$

Substituting the Fourier integral of equation (3.12) for ϕ^* and ϕ in equation (3.17a), one obtains

$$\overline{p_x} = \frac{\hbar}{2\pi}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \left[e^{ikx'}\psi^*(x')\right]k\left[e^{-ikx}\psi(x)\right]dx'\,dx\,dk \qquad (3.17b)$$

where x' and x are two different variables of integration. The factor $k\,e^{-ikx}$ can be expressed as the derivative

$$k\,e^{-ikx} = i\,\frac{\partial}{\partial x}\left(e^{-ikx}\right) \qquad (3.18)$$

and equation (3.17b) then becomes

$$\overline{p_x} = \frac{\hbar}{2\pi}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{ikx'}\psi^*(x')\left(i\,\frac{\partial}{\partial x}\,e^{-ikx}\right)\psi(x)dx'\,dx\,dk \qquad (3.17c)$$

Interchange the order of integration and integrate first over x; integrate by parts and use the fact that the wave function vanishes at the limits, $\psi(\pm\infty) = 0$. Then

$$\overline{p_x} = \int_{-\infty}^{\infty}\left[\frac{1}{2\pi}\int_{-\infty}^{\infty}\psi^*(x')\int_{-\infty}^{\infty} e^{ik(x'-x)}dk\,dx'\right]\frac{\hbar}{i}\,\frac{\partial\psi(x)}{\partial x}\,dx \qquad (3.17d)$$

According to the Fourier integral theorem (refs. 1 and 8), $\psi^*(x)$ is just the inner bracket of equation (3.17d):

$$\psi^*(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\psi^*(x')\int_{-\infty}^{\infty} e^{ik(x'-x)}dk\,dx' \qquad (3.19)$$

This theorem may be derived by substituting equation (3.12) for $\phi(k)$ in equation (3.11) and changing the result to the complex conjugate. Then equation (3.17d) becomes

$$\overline{p_x} = \int_{-\infty}^{\infty}\psi^*(x)\left[\frac{\hbar}{i}\,\frac{\partial}{\partial x}\,\psi(x)\right]dx \qquad (3.17e)$$

an expression for the average value of momentum in terms of ψ^* and the derivative of ψ. At any point x, the integrand is just the product of the momentum p at that point and the probability that the particle is observed at that point, $\psi\psi^*$. Thus the momentum as a function of the position coordinate is

$$p_x = \frac{\hbar}{i\psi}\,\frac{\partial\psi}{\partial x} \qquad (3.20)$$

It is in this sense that the momentum is to be replaced by a derivative operator whenever it appears in any observable quantity to be evaluated from the wave function. The y and z components of momentum in Cartesian coordinates are, of course, represented by the corresponding derivatives with respect to y and z:

$$p_x \rightarrow -i\hbar \frac{\partial}{\partial x}, \qquad p_y \rightarrow -i\hbar \frac{\partial}{\partial y}, \qquad p_z \rightarrow -i\hbar \frac{\partial}{\partial z} \tag{3.21}$$

The operator for a component of momentum squared is obtained by two successive applications of the single-derivative operator. The operator of most interest here is the total energy or the Hamiltonian. For a single particle, this operator is just

$$\begin{aligned} H &= \frac{p_x^2 + p_y^2 + p_z^2}{2m} + V(x,y,z) \\ &= -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x,y,z) \\ &= -\frac{\hbar^2}{2m}\nabla_i^2 + V(q_i) \end{aligned} \tag{3.22}$$

Note that the corresponding operators for the space coordinates x, y, and z are just the coordinates themselves. The potential V may be expressed in any coordinate system other than Cartesian, of course, after which the Laplacian operator ∇^2 is taken to be the appropriate operator in that coordinate system also. Frequently, these operators are expressed in terms of dimensionless coordinates that absorb all constants. Typically, distances are given in units of the Bohr radius a_0, and energy in units of $\hbar^2/2ma_0^2$, in which case the kinetic energy operator becomes simply $-\nabla^2/2$.

One can see from the reciprocal Fourier transform relations between the wave function $\psi(x)$ and the wave number amplitude $\phi(k)$ (eqs. (3.11) and (3.12)) that problems could be worked in momentum space or wave number space equally as well as in position coordinate space. Then the probability of the particle having a wave number k is just $\phi^*\phi$, and all the observables of the system are appropriately weighted with this probability factor. The Cartesian distance coordinate x becomes $i\hbar\, \partial/\partial p_x$ in this system.

Problem 3.2: Use Fourier transform relations to show that the average value of x may be found in terms of wave-number amplitude functions as

$$\bar{x} = \int_{-\infty}^{\infty} \psi^*(x)x\psi(x)dx = \frac{1}{2\pi}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left[e^{-ik'x}\phi^*(k')\right]x\left[e^{ikx}\phi(k)\right]dk'\,dk\,dx$$

and that the value of x for a given momentum p is

$$x = \frac{i}{\phi}\frac{\partial\phi}{\partial k} = \frac{i\hbar}{\phi}\frac{\partial\phi}{\partial p}$$

where $\phi(p) = \hbar^{-1/2}\phi$, the normalized momentum amplitude wave function. Thus, in momentum space, x, y, and z are replaced by the operators

$$x \rightarrow i\hbar \frac{\partial}{\partial p_x}, \quad y \rightarrow i\hbar \frac{\partial}{\partial p_y}, \quad z \rightarrow i\hbar \frac{\partial}{\partial p_z} \tag{3.23}$$

whenever they appear in any observable quantity to be evaluated from the momentum amplitude functions.

Quantum problems are usually worked in coordinate space rather than momentum space because the potential energy functions of interest are usually functions of coordinates only. Thus a much simpler operator results in coordinate space (where the coordinate operators are the coordinates themselves) than in momentum space where some very complex derivative operators would result. Note also that the sign convention on the derivative operators is arbitrary, provided only that the momentum operator in coordinate space and the coordinate operator in momentum space have opposite signs. For example, the Fourier transform relations in equations (3.11) and (3.12) could be expressed equally well with the exponential factors e^{ikx} and e^{-ikx} interchanged. Then one would obtain the momentum operator $i\hbar\ \partial/\partial x$ for p_x and the coordinate operator $-i\hbar\ \partial/\partial p_x$ for x, rather than the relations given in equations (3.21) and (3.23).

To translate these ideas into a physical situation, consider the steady-state wave function of a single particle moving in the x direction, in a region of space where the potential is a constant V_0. The momentum in the x direction is then given by

$$p_0 = \pm[2m(E - V_0)]^{1/2} \tag{3.24}$$

Several solutions to the Schroedinger equation (3.6) are possible, depending on the boundary conditions. One such solution is

$$\psi = C\ e^{ip_0x/\hbar} \tag{3.25}$$

If we operate on this function with the momentum operator and then divide by the wave function as in equation (3.20),

$$p_x = -\frac{i\hbar}{C\ e^{ip_0x/\hbar}} \frac{\partial}{\partial x}\left(C\ e^{ip_0x/\hbar}\right) = p_0 \tag{3.26}$$

we obtain the probable momentum of the wave, the constant p_0. Thus the wave function in equation (3.25) is said to represent a plane wave traveling with a constant momentum p_0, in the positive x direction if p_0 is positive and in the negative x direction if p_0 is negative. (If we had chosen the opposite sign convention, where the momentum operator is $i\hbar\ \partial/\partial x$, then equation (3.25) would merely represent waves traveling in the opposite directions.) Note that, while the momentum is fixed, the probability of locating the particle is everywhere equal so the location is completely indeterminate in accord with the uncertainty principle. In fact, for a single particle, the constant C must be zero (as discussed relative to eq. (3.10)) in order to normalize the probability to unity. More typically, we deal with a directed beam of almost free particles, where the constant C can be normalized to the known current density

$$j = \frac{p_o}{m} \int_{x_o}^{x_o+l} \psi^* \psi \, dx = \frac{C^2 p_o l}{m}$$

where j is the number flux per unit area, p_o/m is the beam velocity, and l is the unit of length. Thus C^2 has the dimensions of particle number per unit volume in this case. Sometimes the integration over the beam cross-sectional area that gives the total current is used, in which case the normalization constant squared has the dimensions of particles per unit length of beam.

Generally, the momentum is not a constant, of course, but changes with the potential of the region in which the particle moves. Again, if the particle is restricted to one-dimensional motion for simplicity, the wave function has the form

$$\psi \sim C \, e^{i[2m(E-V)]^{1/2} x/\hbar} \tag{3.27}$$

where the constant E is the total energy and the potential V and amplitude C are both functions of x. If V is relatively constant over a region large compared with the wavelength, $\hbar[2m(E - V)]^{-1/2}$ (which corresponds to classical behavior of the particle), the solution to the Schroedinger equation has the same form as equation (3.25) with nearly constant C and with p_o representing the slowly varying quantity $[2m(E - V)]^{1/2}$. Any arbitrary potential function can be approximated by a series of step functions, each giving a solution for the wave function of the form of equation (3.25). These solutions may be interfaced with one another by matching the magnitude and the first derivative of the wave function at each interface to give an approximation to the true wave function. Matching the wave functions conserves the probable number density at that point and makes number density a continuous function; matching the derivatives conserves the probable momentum at that point and makes momentum a continuous function. In this manner, the character of the wave function for any arbitrary potential can be physically assessed, even though the analytic expression for that function may be complex. For example, figure 3.1 shows the form of the wave function for a beam of free particles crossing a potential hump of some sort. Only the real part of ψ is shown, but an imaginary part 90° out of phase with the real part can be visualized out of the plane

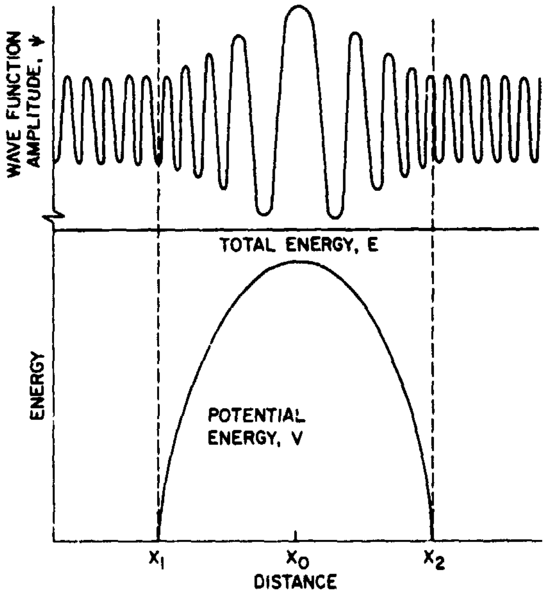

Figure 3.1.- Wave function for a beam of free particles crossing a potential hump; $\psi \sim Re\left\{C \, e^{i[2m(E-V)]^{1/2} x/\hbar}\right\}$.

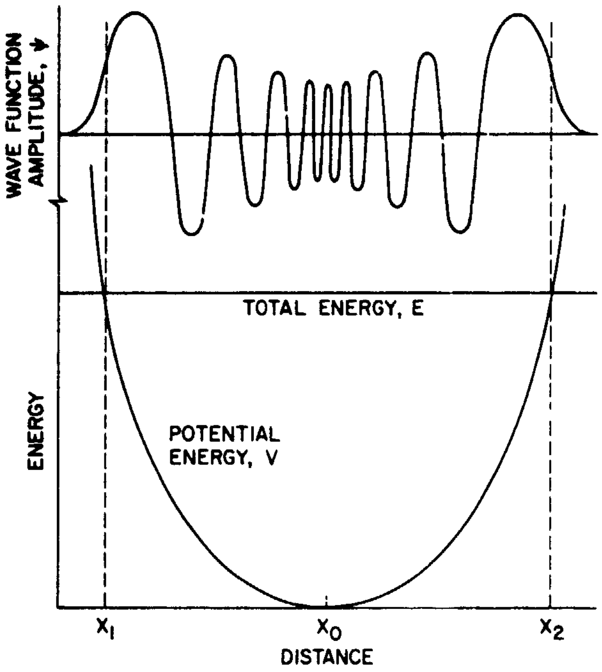

Figure 3.2.- Wave function for a bound particle in steady state in a potential well:

$x < x_1, \quad \psi \sim C\, e^{[2m(V-E)]^{1/2}x/\hbar}$

$x_1 < x < x_2, \quad \psi \sim C \cos[2m(E-V)]^{1/2}x/\hbar$

$x_2 < x, \quad \psi \sim C\, e^{-[2m(V-E)]^{1/2}x/\hbar}$

of the figure. Up to point x_1, ψ has a constant amplitude and wavelength characteristic of the completely free beam. At x_1, the wavelength and the amplitude both increase as the beam loses momentum and bunches up over the potential hump. At the potential maximum, the wavelength and amplitude decrease again until they return to their original value at x_2. In the step function approximation, C and V are piecewise constant, and the result of operating on the wave function with the momentum operator and dividing by the wave function is a real quantity, corresponding to the fact that the momentum of the beam is everywhere observable:

$$-\frac{i\hbar}{\psi}\frac{\partial\psi}{\partial x} \approx [2m(E-V)]^{1/2} \qquad (3.28)$$

In many situations, the wave function is needed for particles that are bound and move about in some sort of potential well. Even in a gas where the particles are relatively free, the particles are eventually bound by the walls of the container, for example. The particle then reflects from the region where $V-E$ becomes positive, as illustrated in figure 3.2, again for one-dimensional motion. In this case the reflected wave is added to the transmitted wave, which in steady state sets up a standing wave. Again, for the slowly varying potential case, the wave function has the character of cosine or sine waves if $E > V$:

$$\psi \sim C\left\{e^{i[2m(E-V)]^{1/2}x/\hbar} \pm e^{-i[2m(E-V)]^{1/2}x/\hbar}\right\} \qquad (3.29a)$$

but decreases as an exponential in the region where $V > E$:

$$\psi \sim C\, e^{\pm[2m(V-E)]^{1/2}x/\hbar} \qquad (3.29b)$$

The negative exponent must be used if x increases and the positive exponent if x decreases. Otherwise, the wave function becomes infinite at the boundaries ($x \to \pm\infty$) and the probability everywhere vanishes (i.e., $C = 0$). In figure 3.2, a standing wave is depicted between x_1 and x_2 with small amplitude and short wavelength near the potential minimum, where the particle has the largest velocity and the least probability of being located, and with large amplitude and long wavelength near the classical turning points x_1 and x_2, where the particle has the least velocity and the largest probability of being located. Outside the region x_1 to x_2, the wave function is nonoscillating and has an exponentially decreasing amplitude.

Note that the momentum operator leads to an imaginary quantity with such a function. For example, if $E > V$ and $\psi \sim \cos kx$,

$$-\frac{i\hbar}{\psi}\frac{\partial\psi}{\partial x} = -i\hbar k \cos kx \sin kx \tag{3.30a}$$

while, if $E < V$ and $\psi \sim e^{-kx}$,

$$-\frac{i\hbar}{\psi}\frac{\partial\psi}{\partial x} = -i\hbar k \tag{3.30b}$$

This corresponds to the fact that momentum is unobservable in this system; that is, one cannot tell whether the bound particle in steady state is approaching the potential barrier or receding from it. However, note that kinetic energy and probability both have finite real values in the region $V > E$. The skin depth where the probability is appreciable in this region is very thin if $V >> E$, of course.

A system of gas particles in a box is modelled well by assuming that the box is potential free and that the walls are a sudden discontinuous potential rise to $+\infty$. Then the wave functions for such particles are precisely the sine and cosine waves that match these boundary conditions; only in the region of the wall, where the barrier is not truly discontinuous, would these wave functions be somewhat imprecise. Gas particles move in three dimensions, of course, but usually in relatively potential free space, in which case the three-dimensional wave function can be simply expressed as a product of one-dimensional wave functions of the type discussed above:

$$\psi(x,y,z) = \psi(x)\psi(y)\psi(z) = C\, e^{i(k_x x + k_y y + k_z z)} \tag{3.31}$$

In many cases of interest, particles are bound in a potential well, with boundary conditions best described in spherical, or sometimes cylindrical, coordinates. In these coordinate systems, the momentum operators are no longer simple first derivatives, as in equation (3.21), but must be constructed so that the value of an observable quantity given by the operator is a real quantity. A number is purely real if, and only if, it equals its complex conjugate. Thus the operator $\tilde{O}$ which corresponds to an average observable quantity $\overline{O}$ must satisfy the relation

$$\overline{O} = \int \psi^*(\tilde{O}\psi)\,d\tau = \int \psi(\tilde{O}^*\psi^*)\,d\tau = \overline{O}^* \tag{3.32}$$

A class of operators called Hermitian have this property. Actually, Hermitian operators may have yet more general properties with respect to an entire class of functions. These properties are discussed briefly in appendix 3-A, along with some comments on wave functions that have spherical or cylindrical symmetry, so that the reader may refresh his knowledge in these basic quantum topics.

3.4 QUANTIZED FREE PARTICLES

A particle moving in potential free space ($V = 0$) with momentum $\vec{p} = \vec{k}\hbar$ has a wave function that obeys

$$\nabla^2\psi + k^2\psi = 0 \tag{3.33}$$

The solution is determined by the boundary conditions, of course. If boundary conditions consistent with a plane wave are assigned, a traveling wave solution in three dimensions takes the form

$$\psi = C\, e^{\pm i\vec{k}\cdot\vec{r}} \tag{3.34}$$

where $\vec{k}$ and $\vec{r}$ are now vector quantities giving the wave number and position in three orthogonal coordinate directions. The steady-state, standing wave function that fits the given boundary conditions is formed from a linear superposition of the traveling wave solutions above; these are expressible as products of cosine or sine factors, for example,

$$\psi = C \cos(k_1 r_1) \cos(k_2 r_2) \cos(k_3 r_3) \tag{3.34a}$$

where the subscripts 1, 2, and 3 represent vector components in the x, y, and z directions, respectively. Consistent with the choice of the plane-wave solution, a boxlike volume with sides λ_1, λ_2, and λ_3 is imposed as the boundary. (Different boundary conditions are required for a differently shaped standing wave.) The standing wave must return to its original value after a distance $2\lambda_i$ (one complete traverse of the box in both directions); therefore,

$$2k_i\lambda_i = \frac{4\pi p_i\lambda_i}{h} = 2\pi n_i \tag{3.35}$$

where n_i may be any integer from 0 to ∞ and is a quantum number that represents the steady-state translational wave function of a particle. The energy of the particle in steady state is thus

$$\varepsilon = \frac{p^2}{2m} = \frac{h^2}{8m}\left[\left(\frac{n_1}{\lambda_1}\right)^2 + \left(\frac{n_2}{\lambda_2}\right)^2 + \left(\frac{n_3}{\lambda_3}\right)^2\right] \tag{3.36}$$

The usual procedure at this point is to combine all energies lying within a range $d\varepsilon$ and compute how many different combinations of the n_i give this same energy; this number is the degeneracy g. We can equally well count each state separately with unit degeneracy. The partition function for the translational motion is then (see ch. 1)

$$Q = \sum_i e^{-\varepsilon_i/kT} = \sum_{n_1=0}^{\infty} e^{-\alpha_1{}^2 n_1{}^2} \sum_{n_2=0}^{\infty} e^{-\alpha_2 n_2{}^2} \sum_{n_3=0}^{\infty} e^{-\alpha_3{}^2 n_3{}^2} \tag{3.37a}$$

where $\alpha_i{}^2$ is $h^2/8mkT\lambda_i{}^2$. Because α_i is normally very small compared with unity, the sums may be approximated with an integral

$$\sum_{n=0}^{\infty} e^{-\alpha^2 n^2} \simeq \int_0^\infty e^{-\alpha^2 x^2}\, dx = \frac{\sqrt{\pi}}{2\alpha} \tag{3.38}$$

Thus, the partition function of the free particle becomes

$$Q = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \lambda_1 \lambda_2 \lambda_3 = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V \tag{3.37b}$$

where V is the potential free volume available to the particle. We state without proof that the same result as equation (3.37b) would be found for an arbitrarily shaped volume if the appropriate standing wave function for that shape were used (ref. 2).

Problem 3.3: Show that for a gas of H_2 molecules at normal temperature and density, and with scattering cross sections the order of 10^{-15} cm^2, α_i^2 is the order of 10^{-6}. Thus, the integral in equation (3.38) is a good approximation for the sums involved in the partition function. Note that the approximation improves as density and scattering cross section decrease and temperature and molecular weight increase.

3.5 CLASSICAL FREE PARTICLES

The spacing between energy levels of a free particle is normally small compared with kT, at least for moderate values of the quantum number n:

$$\frac{\varepsilon}{kT} = \alpha^2 n^2 \ , \qquad \frac{\Delta\varepsilon}{kT} \simeq 2\alpha^2 n \tag{3.39}$$

In such cases, one expects the correspondence principle to apply and the classical and quantum results should be the same. The classical partition function for the free particle is

$$Q = \frac{1}{h^3} \int \dots \int e^{-H/kT}\, dx_1\, dx_2\, dx_3\, dp_1\, dp_2\, dp_3 \tag{3.40}$$

The Hamiltonian expression for the energy of a free particle is

$$H = \frac{p_1{}^2 + p_2{}^2 + p_3{}^2}{2m} \tag{3.41}$$

Performing the integrations over x_1, x_2, and x_3 yields the free volume V over which the Hamiltonian is given by equation (3.41). Thus

$$Q = \frac{V}{h^3}\left(\int_{-\infty}^{\infty} e^{-p_i^2/2mkT}\, dp_i\right)^3 = \frac{V}{h^3}\,(2\pi mkT)^{3/2} \tag{3.42}$$

the same result obtained by the quantum arguments, equation (3.37b).

3.6 THERMODYNAMIC PROPERTIES OF INERT GASES COMPOSED OF CLASSICAL PARTICLES

For gas particles with no internal degrees of freedom, Q/N, from equation (3.42), is

$$\frac{Q}{N} = \frac{V}{Nh^3}\,(2\pi mkT)^{3/2} \tag{3.43}$$

The energy is then

$$E - E_o = RT^2\left(\frac{\partial\, ln\, Q}{\partial T}\right)_V = \frac{3}{2}RT \tag{3.44}$$

and the specific heat at constant volume

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{2}R \tag{3.45}$$

The entropy becomes

$$\begin{aligned} S &= R\, ln\, \frac{Q}{N} + RT\left(\frac{\partial\, ln\, Q}{\partial T}\right)_V + R \\ &= R\, \ln\left[\frac{V}{Nh^3}\,(2\pi mkT)^{3/2}\right] + \frac{5}{2}R \end{aligned} \tag{3.46}$$

and the free energy is given by

$$\begin{aligned} F - E_o &= -RT\left(ln\, \frac{Q}{N} + 1\right) \\ &= -RT\left[ln\, \frac{V}{Nh^3}\,(2\pi mkT)^{3/2} + 1\right] \end{aligned} \tag{3.47}$$

The pressure is

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{RT}{V} \tag{3.48}$$

the familiar ideal gas law. The enthalpy H and free enthalpy G are simply evaluated by adding pV to equation (3.44) and (3.47), respectively.

So far, the gas has been treated as a collection of independent particles. This model is a good approximation for dilute gases where the particles have negligible interaction except during collisions, which occupy only a small fraction of time. The above results are later modified to account for dispersion forces in very dense gases (ch. 8). Even in the dilute gas phase, however, collections of electrons and photons are found to obey somewhat different statistics than the Maxwell-Boltzmann statistics used thus far. The differences introduced by quantum statistics are considered next.

3.7 THERMODYNAMIC PROPERTIES OF INERT GASES COMPOSED OF QUANTUM PARTICLES

The thermodynamic properties of gases composed of quantized gas particles are slightly different than the properties deduced for a gas of Maxwell-Boltzmann particles because the statistical distributions are different. The deviation from the Maxwell-Boltzmann distribution is called degeneration (when used in this sense, the term has no connection with the concept of a degenerate energy level). The normalization parameter α is an index of this degeneration. One readily sees that if α is very large, both the Einstein-Bose and Fermi-Dirac distributions become Maxwell-Boltzmann as the factor ±1 is negligible compared with $e^{\alpha+\beta\varepsilon_i}$. In this state, $n_i \ll g_i$ and the degenerate energy levels are not filled, which means that the state is one of high dilution and high energy. The smaller the value of α, the larger will be the effect of degeneration. The minimum value α can have is zero for the Einstein-Bose gas since negative n_i is meaningless, while α can go as far as $-\infty$ for the Fermi-Dirac gas.

Before investigating quantum effects on thermodynamic properties of gases, we derive general formulas for the kinetic energy and pressure of weakly interacting quantized particles without internal energy. At any given instant, each particle is in one of the available steady-state eigenvalues given by equation (3.36). Consider the special case of a cubical box with equal sides $\lambda_1 = \lambda_2 = \lambda_3 = V^{1/3}$. The energy of n noninteracting particles in this box is

$$E = \sum_{i=1}^{n} \varepsilon_i = \frac{h^2}{8mV^{2/3}} \sum_i \left(n_{1i}^2 + n_{2i}^2 + n_{3i}^2\right) \tag{3.49}$$

A fundamental theorem of quantum mechanics states that reversible adiabatic variations of external parameters do not change the quantum numbers. In practical terms, this means that if the perturbations are small enough, the quantum states are perturbed so little that the summation of squared quantum numbers in equation (3.49) is essentially constant. In this limit, then

$$E = const/V^{2/3} \tag{3.50a}$$

The same result occurs for any arbitrarily shaped volume (see ref. 2), and the result is also the same as for classical ideal gases in reversible adiabatic change of state,

$$E = \frac{3}{2} RT = \frac{3}{2} pV = \frac{const}{V^{\gamma-1}} = \frac{const}{V^{2/3}} \qquad (3.50b)$$

since γ, the ratio of specific heats, is just 5/3 for a gas of monatomic particles considered here.

A completely general relation for pressure follows from equations (1.9) and (3.50):

$$p = -\left(\frac{\partial E}{\partial V}\right)_S = \frac{2}{3} \frac{E}{V} \qquad (3.51)$$

This relation is useful later in obtaining the equation of state for degenerate gases.

Define a vector magnitude squared ν^2 as the sum of all squared quantum numbers:

$$\nu^2 = \sum_{i=1}^{n} \left(n_{1i}^2 + n_{2i}^2 + n_{3i}^2\right) \qquad (3.52)$$

Then the number of states with energy E or less is just the number of lattice points in a volume 1/8 the volume a sphere of radius ν, or $\pi\nu^3/6$ (i.e., just the volume of the spherical quadrant in which all quantum numbers are positive). From equation (3.49) and (3.52), one obtains as the total number of quantum states with energy less than E:

$$G = (2s + 1) \frac{4\pi V (2mE)^{3/2}}{3h^3} \qquad (3.53)$$

where the result is multiplied by $(2s + 1)$ to account for the degeneracy of spin states occurring when the gas particles have spin quantum number s (see ch. 4). The degeneracy of states with energy levels between E and $E + dE$ is thus

$$g = \frac{dG}{dE} dE = \frac{(2s + 1) 2\pi V (2m)^{3/2} E^{1/2} \, dE}{h^3} \qquad (3.54)$$

Problem 3.4: Show that the total number of degenerate states available to gas particles of normal mass and temperature is the order of 10^{24} per cm^3 so that, at normal gas densities, only a fraction of the degenerate states is occupied.

First consider the case of negligible degeneration. The factor $e^{-\alpha}$ is given by normalization to the total number of particles n as

$$n = (2s + 1) \frac{2\pi V (2mkT)^{3/2}}{h^3} e^{-\alpha} \int_0^\infty e^{-x} x^{1/2} \, dx \qquad (3.55)$$

where the variable of integration $x = E/kT$. Thus

$$e^{-\alpha} = \frac{nh^3}{(2s + 1)V(2\pi mkT)^{3/2}} \tag{3.56}$$

is the degeneration factor obtained when the quantized particles obey Maxwell-Boltzmann statistics. If this value of $e^{-\alpha}$ is substituted in the distribution function, the usual Maxwell velocity distribution law of kinetic theory is obtained. The dimensionless quantity on the right-hand side in equation (3.56) is defined as y, for ease in formulating the expansions that follow, and it is a very small quantity for usual values of m, T, and V/n.

Next consider the Einstein-Bose gas. The degeneracy factor g is the same as given by equation (3.54), but the distribution function now has a different form:

$$y = \frac{nh^3}{(2s + 1)V(2\pi mkT)^{3/2}} = \frac{1}{\Gamma(3/2)} \int_0^\infty \frac{x^{1/2}\,dx}{e^{\alpha+x} - 1} \tag{3.57}$$

Digress for a moment to examine the integrals

$$U(\alpha,r) = \frac{\quad}{\Gamma \qquad 1)} \int_0^\infty \frac{x^r\,dx}{e^{\alpha+x} - 1} \tag{3.58}$$

The values of r of interest are 1/2 and 3/2. Expand the integrand in equation (3.58) as

$$\frac{x^r}{e^{\alpha+x} - 1} = x^r \sum_{n=1}^{\infty} e^{-n(\alpha+x)} \tag{3.59}$$

Then

$$\begin{aligned} U(\alpha,r) &= \frac{1}{\Gamma(r + 1)} \sum_{n=1}^{\infty} e^{-n\alpha} \int_0^\infty x^r e^{-nx}\,dx \\ &= \sum_{n=1}^{\infty} \frac{e^{-n\alpha}}{n^{r+1}} \end{aligned} \tag{3.60}$$

Note that the series converges for all $\alpha \geq 0$. The value of y given by equation (3.57) can thus be expressed as the series

$$y = U\left(\alpha, \frac{1}{2}\right) = e^{-\alpha} + \frac{e^{-2\alpha}}{2^{3/2}} + \frac{e^{-3\alpha}}{3^{3/2}} + \ldots \tag{3.61}$$

The quantity $e^{-\alpha}$ may be obtained by successive approximation. The first approximation is

$$e^{-\alpha} = y \tag{3.62a}$$

which gives just the Maxwell-Boltzmann law. Substituting this value of $e^{-\alpha}$ in all but the first term of the series in equation (3.61) yields a second approximation to terms of order y^2:

$$e^{-\alpha} = y - \frac{y^2}{2^{3/2}} \tag{3.62b}$$

Similarly, substituting the second approximation in all but the first term of the series yields a third approximation to terms of order y^3:

$$e^{-\alpha} = y - \frac{y^2}{2^{3/2}} + \left(\frac{1}{4} - \frac{1}{3^{3/2}}\right) y^3 - \ . \ . \ . \tag{3.62c}$$

The process can easily by continued to higher-order terms, but the third approximation is sufficiently precise for most applications.

Now calculate the energy and pressure for the Einstein-Bose gas:

$$\left.\begin{aligned} E &= \int_{\varepsilon=0}^{\varepsilon=\infty} \varepsilon\ dn = \frac{(2s+1)V(2\pi mkT)^{3/2}}{h^3}\ \frac{kT}{\pi^{1/2}} \int_0^\infty \frac{x^{3/2}\,dx}{e^{\alpha+x} - 1} \\ E &= \frac{3}{2}\,nkT\ \frac{U(\alpha,3/2)}{y} \\ &= \frac{3}{2}\,nkT\ \frac{U(\alpha,3/2)}{U(\alpha,1/2)} \end{aligned}\right\} \tag{3.63}$$

The ratio $U(\alpha,3/2)/U(\alpha,1/2)$ corrects the classical energy to account for the effects of degeneration.

The pressure is obtained from equation (3.51) as

$$p = \frac{2}{3}\,\frac{E}{V} = \frac{nkT}{V}\,\frac{U(\alpha,3/2)}{U(\alpha,1/2)} \tag{3.64}$$

so the same ratio corrects the classical pressure for effects of degeneration.

Consider weak degeneration where the third approximation is sufficient

$$\left(\frac{2E}{3nkT}\right) = \left(\frac{pV}{nkT}\right) = \frac{1}{y}\left(e^{-\alpha} + \frac{e^{-2\alpha}}{2^{5/2}} + \frac{e^{-3\alpha}}{3^{5/2}} + \ . \ . \ .\right) \tag{3.65a}$$

then, if we substitute for $e^{-\alpha}$, the correction factor becomes

$$\left(\frac{2E}{3nkT}\right) = \left(\frac{pV}{nkT}\right) = 1 - 0.1768y - 0.0033y^2 - \ . \ . \ . \tag{3.65b}$$

For H_2 at standard conditions, $y \approx 10^{-5}$, so both energy and pressure take their classical values. For other gases, the value of y is even smaller because of the larger mass involved. Only at very low temperatures will strong degeneration occur. To see how low these temperatures must be, consider the minimum value of α that can occur for an Einstein-Bose gas, namely, $\alpha = 0$. Then the series expression for y converges to a finite limit

$$y = 1 + \frac{1}{2^{3/2}} + \frac{1}{3^{3/2}} + \frac{1}{5^{3/2}} + \ldots = 2.612 \qquad (3.66)$$

and the temperature at this limit is

$$T_o = \frac{h^2}{2\pi mk}\left[\frac{n}{2.612V(2s + 1)}\right]^{2/3} \qquad (3.67)$$

(called the critical temperature). One might conclude that lower temperatures are not possible for an Einstein-Bose gas since α cannot be less than zero in this case. However, this conclusion is not correct; the value of n is actually given by a summation rather than the integral, and the summation terms have positive values for n_i for all T even when $\alpha = 0$. At temperatures below critical, an increasing number of molecules are found in the ground state until, finally, at $T = 0$ all molecules are in the ground state. On compression or expansion at constant T below critical, pressure does not vary and the gas behaves like a two-phase system, a behavior called "condensation" of the Einstein-Bose gas.

He^4 is the only molecule that provides a perceptible value of T_O, and even in this case the gas liquifies at 4° K, before the critical point is reached, and the assumption that the system is composed of weakly interacting particles is no longer valid. The critical temperature given by equation (3.67) with the liquid He mol volume equal to 27.6 cc is T_O = 3.13° K, quantitatively somewhat different than the observed λ point of liquid He, 2.19° K. (The properties of liquid He drastically change at the λ point. For example, HeI condenses to HeII below the λ point and is then observed to have nearly zero viscosity, zero surface tension, and fantastically high thermal conductivity - hundreds of times the value of Cu and thousands of times larger than HeI). Nevertheless, the condensation effect predicted for a gas of weakly interacting bosons does qualitatively describe many of the observed features of HeII the simple model described needs to be corrected primarily for perturbation effects of nearby neighbors in the liquid phase.

In a practical sense, aside from understanding the behavior of HeII, the quantum model of a boson gas is not very useful. However, the quantum model of a gas composed of fermions, which obey Fermi-Dirac statistics, is exceedingly useful because electrons free to move in space or in a crystal lattice of conducting material comprise such a gas. In this case, the mathematical model develops exactly the same as for the boson except that the negative sign in the denominator of the integrand becomes a plus:

$$y = \frac{Nh^3}{(2s + 1)V(2\pi mkT)^{3/2}} = \frac{1}{\Gamma(3/2)} \int_0^\infty \frac{x^{1/2}\,dx}{e^{\alpha+x} + 1} \tag{3.68}$$

For this case, examine the integrals

$$V(\alpha,r) = \frac{1}{\Gamma(r + 1)} \int_0^\infty \frac{x^{1/2}\,dx}{e^{\alpha+x} + 1} \tag{3.69}$$

for the range of α from $-\infty$ to $+\infty$. Consider first $\alpha > 0$ and, subsequently, $\alpha < 0$.

For $\alpha > 0$, expanding the integrand as before one obtains

$$y = V\left(\alpha, \frac{1}{2}\right) = \sum_{n=1}^{\infty} \frac{(-1)^{n+1} e^{-n\alpha}}{n^{r+1}} = e^{-\alpha} - \frac{e^{-2\alpha}}{2^{3/2}} + \frac{e^{-3\alpha}}{3^{3/2}} - \dots$$

which, by successive approximation, leads to a formula similar to the boson gas case:

$$e^{-\alpha} = y + \frac{y^2}{2^{3/2}} + \left(\frac{1}{4} - \frac{1}{3^{3/2}}\right) y^3 + \dots \tag{3.70}$$

For $\alpha < 0$, the series above diverges. Sommerfeld (ref. 9) developed a series in inverse powers of α which converges only for $\alpha < -1$ (see also the review of degenerate gas relations in ref. 10). To terms of second order, this series is

$$V(\alpha,r) = \frac{(-\alpha)^{r+1}}{\Gamma(r + 2)} \left[1 + \frac{\pi^2}{6} \frac{r(r + 1)}{\alpha^2} + \dots\right] \tag{3.71}$$

which can be used when $\alpha \ll -1$. Thus,

$$y \simeq \frac{4(-\alpha)^{3/2}}{3\sqrt{\pi}} \left(1 + \frac{\pi^2}{8\alpha^2} + \dots\right) \tag{3.72}$$

and

$$(-\alpha) \simeq \left(\frac{3\sqrt{\pi}\,y}{4}\right)^{2/3} \left(1 + \frac{\pi^2}{8\alpha^2} + \dots\right)^{-2/3} \simeq \left(\frac{3\sqrt{\pi}\,y}{4}\right)^{2/3} \left(1 - \frac{\pi^2}{12\alpha^2} + \dots\right) \tag{3.73}$$

Again, by use of successive approximation, we obtain for a first approximation

$$(-\alpha) = \left(\frac{3\sqrt{\pi}\,y}{4}\right)^{2/3} \tag{3.74}$$

and, for a second approximation,

$$(-\alpha) = \left(\frac{3\sqrt{\pi}\,y}{4}\right)^{2/3}\left[1 - \frac{\pi^2}{12}\left(\frac{4}{3\sqrt{\pi}\,y}\right)^{4/3} + \ldots\right] \tag{3.75}$$

which is sufficiently good for very strong degeneration, $\alpha << -1$.

Proceeding as before, we find that the expressions for energy and pressure have the same form for the fermion gas as for the boson gas except that the functions $V(\alpha,r)$ replace the functions $U(\alpha,r)$:

$$\frac{2E}{3nkT} = \frac{pV}{nkT} = \frac{V(\alpha,3/2)}{V(\alpha,1/2)} \tag{3.76}$$

For the case of weak degeneration, the expansions are the same as before except for an alternation in sign of the series terms

$$\frac{2E}{3nkT} = \frac{pV}{nkT} = (1 + 0.1768y - 0.0033y^2 + \ldots) \tag{3.77}$$

Physically, the effect of degeneration is like an attractive force between boson particles which reduces the pressure and like a repulsive force between fermion particles which increases the pressure. For strong degeneration of fermions, the Sommerfeld approximation is used:

$$\begin{aligned} E &= \frac{3}{2}\,nkT\,\frac{V(\alpha,3/2)}{V(\alpha,1/2)} \\ &\simeq \frac{3}{2}\,nkT(-\alpha)\,\frac{\Gamma(5/2)}{\Gamma(7/2)}\,\frac{\left(1 + \frac{5\pi^2}{8\alpha^2} + \ldots\right)}{\left(1 + \frac{\pi^2}{8\alpha^2} + \ldots\right)} \\ &\simeq \frac{3}{5}\,nkT(-\alpha)\left(1 + \frac{\pi^2}{2\alpha^2} + \ldots\right) \end{aligned} \tag{3.78}$$

Substituting for α from equation (3.75) one obtains, to terms of order $y^{-2/3}$

$$E \simeq \frac{3}{5}\,nkT\left(\frac{3\sqrt{\pi}\,y}{4}\right)^{2/3}\left[1 + \frac{5\pi^2}{12}\left(\frac{4}{3\sqrt{\pi}\,y}\right)^{4/3} + \ldots\right] \tag{3.79}$$

From equation (3.68), $y^{2/3}$ varies as T^{-1}:

$$\left(\frac{3\sqrt{\pi}\,y}{4}\right)^{2/3} = \frac{h^2}{2mkT}\left[\frac{3n}{(2s + 1)4\pi V}\right]^{2/3} \tag{3.80}$$

so at absolute zero temperature the fermion gas still has finite energy and pressure

$$E = \frac{3pV}{2} = \frac{3nh^2}{10m}\left[\frac{3n}{(2s+1)4\pi V}\right]^{2/3} + \frac{\pi^2 nm}{2h^2}\left[\frac{(2s+1)4\pi V}{3n}\right]^{2/3} k^2T^2 + \ldots \qquad (3.81)$$

The first term on the right side of equation (3.81) is just the zero point energy of a Fermi-Dirac gas. The constant volume specific heat vanishes at zero temperature instead of being finite ($3nk/2$) as for the Maxwell-Boltzmann gas:

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v = \frac{\pi^2 nm}{h^2}\left[\frac{(2s+1)4\pi V}{3n}\right]^{2/3} k^2T + \ldots \qquad (3.82)$$

The existence of E_o follows from the Pauli exclusion principle, of course. Only $(2s + 1)$ particles can occupy the lowest state, the next $(2s + 1)$ must go into the next highest state, and so on. The sum of all these energies is E_o.

Problem 3.5: Derive the expression for E_o by normalizing the distribution at absolute zero temperature so that all levels up to ε_m are filled:

$$n = \int_o^{\varepsilon_m} dg = \frac{(2s+1)2\pi V(2m)^{3/2}}{h^3}\int_o^{\varepsilon_m} \varepsilon^{1/2}\, d\varepsilon$$

Then, with the value of ε_m so obtained, calculate

$$E_o = \int_o^{\varepsilon_m} \varepsilon\, dn = \frac{(2s+1)2\pi V(2m)^{3/2}}{h^3}\int_o^{\varepsilon_m} \varepsilon^{3/2}\, d\varepsilon$$

Problem 3.6: Calculate the value of y and α for Ag at 300° K. Use $N/V = 5.9\times10^{22}$ electrons/cm^3 and spin quantum number $s = 1/2$. Show that y is the order of 10^3 rather than 10^{-5} as for ordinary gases and that $(-\alpha)$ is the order of 10^2, which is large enough for the Sommerfeld expansions to become reasonably accurate. Also find the contribution of the free electrons to the specific heat C_v and show that it is the order of 10^{-2} times the specific heat of a normal nondegenerate gas.

Problem 3.7: To what temperature would Ag need to be raised (assuming that the crystal did not melt) so that the electron gas would be reasonably nondegenerate and contribute approximately $3nk/2$ to the specific heat? Note that according to equation (3.77) y must be the order of 1 or less.

3.8 CONCLUDING REMARKS

The uncertainty principle is fundamental to the quantum behavior of matter and follows from the mathematical description, in terms of Fourier transform integrals, of a particle whose motion is described by a wave but which is simultaneously localized in space. This principle establishes the quantum cell size in phase space and, consequently, the numerical equivalence between the classical phase integrals and the partition functions, which allow us to evaluate all thermodynamic properties of a system of particles. In addition, the uncertainty principle establishes the derivative operators that allow us to evaluate functions of momentum in physical space from the quantum wave functions or, conversely, to evaluate functions of position in momentum space from the momentum amplitude functions, which are Fourier transforms of the wave functions. These quantum formulations remove time as a parameter from steady-state problems, and these may then become easier to solve than in the corresponding classical formulations, even when the classical model is a good approximation.

In most gases of interest, the particles behave classically and the statistics lead to the Maxwell-Boltzmann distribution for the equilibrium state of a system of particles. However, at very high density and/or very low temperature, the quantum effects of gas degeneration are sometimes observed. If the gas is composed of particles with an odd number multiple of half integer spin (i.e., the particles consist of an odd number of fundamental particles), the particles cannot simultaneously occupy the same quantum state and they then obey Fermi-Dirac statistics. At low temperature or high density, these particles behave as though they repel one another. Effects of this repulsion are observed in gaslike, high-density conduction electrons in metals, for example. If the gas is composed of particles with an even number multiple of half integer spin (i.e., the particles consist of an even number of fundamental particles), the particles can simultaneously occupy the same quantum state and they then obey Bose-Einstein statistics. At low temperature or high-density, these particles behave as though they attract one another. Effects of this condensation are noticed in the low-temperature behavior of helium, for example.

The analysis of the normally weak quantum effects mentioned above reminds us that the models established for the partition functions and the derivative thermodynamic properties are, after all, just models. Despite the very good accuracy these models attain over a broad range of variables, all have approximations that eventually limit their usefulness when certain parameters of state are extended far enough.

APPENDIX 3-A: HERMITIAN OPERATORS AND WAVE FRONTS IN CYLINDRICAL AND SPHERICAL COORDINATES

In section 3.3, we found that by expressing the wave function as a Fourier integral in momentum space, a component of momentum could be expressed as an operator acting on the wave function, all divided by the wave function:

$$-\frac{i\hbar}{\psi}\frac{\partial\psi}{\partial x} = p_x \qquad \text{(3-A1)}$$

A similar operator relation obtains for observable quantities other than momentum: for example, some arbitrary function of both momentum and position such as total energy. Such operator relations may be expressed generally as

$$\tilde{O}\psi = O\psi \qquad \text{(3-A2)}$$

where $\tilde{O}$ corresponds to the operator and O corresponds to the observable quantity, which is a real number.

Multiply equation (3-A2) by ψ^* and integrate over all space to obtain

$$\int\psi^*(\tilde{O}\psi)d\tau = \int\psi^* O\psi\, d\tau = \bar{O} \qquad \text{(3-A3a)}$$

Also take the complex conjugate of equation (3-A2), multiply by ψ, and integrate over all space:

$$\int\psi(\tilde{O}^*\psi^*)d\tau = \int\psi O^*\psi^*\, d\tau = \bar{O}^* \qquad \text{(3-A3b)}$$

But since O is everywhere a real quantity, the average value $\bar{O}$ must also be real, which is true if and only if $\bar{O}$ equals its complex conjugate $\bar{O}^*$. Thus the equality of equation (3.32) must obtain

$$\int\psi^*(\tilde{O}\psi)d\tau = \int\psi(\tilde{O}^*\psi^*)d\tau \qquad \text{(3-A4)}$$

Any operator that satisfies this equality is said to be Hermitian with respect to the function ψ. Often the operators of interest in quantum mechanics are Hermitian with respect to an entire set of wave functions as well as to a single member of this set. For example, a system in steady state may generally occupy any one of a number of different steady states a, b, c, etc. that have different energies and different wave functions, ψ_a, ψ_b, ψ_c, etc. These are orthogonal to one another (ref. 3) and may be normalized so that

$$\int\psi_j^*\psi_i\, d\tau = \delta_{ij}(=1 \text{ if } i=j,\ =0 \text{ if } i\neq j) \qquad \text{(3-A5)}$$

Equation (3-A5) merely expresses the physical requirement that the integral of the probability over all possible configuration space is unity, and that the probability vanishes that the system is simultaneously in steady state i and a different steady state j.

The same operator $\tilde{O}$ will generally result in different values of the observable O_a, O_b, O_c, etc., depending on the state of the system

$$\tilde{O}\psi_i = O_i\psi_i \tag{3-A6}$$

Multiply equation (3-A6) by ψ_j^* and integrate over all space to obtain

$$\int\psi_j^*(\tilde{O}\psi_i)d\tau = \int\psi_j^* O_i\psi_i\, d\tau = \overline{O_{ij}} \tag{3-A7a}$$

where $\overline{O_{ij}}$ represents the average value of O during a time-dependent transition from state i to state j. (Such transition quantities are discussed in chapters 5 through 8 when perturbation coupling between states is considered, for example.) Similarly, in the reverse transition from state j to state i,

$$\int\psi_i^*(\tilde{O}\psi_j)d\tau = \int\psi_i^* O_j\psi_j\, d\tau = \overline{O_{ji}} \tag{3-A7b}$$

the complex conjugates of the above relations may also be formed as

$$\int\psi_j(\tilde{O}^*\psi_i^*)d\tau = \int\psi_j O_i^*\psi_i^*\, d\tau = \overline{O}_{ij}^* \tag{3-A7c}$$

$$\int\psi_i(\tilde{O}^*\psi_j^*)d\tau = \int\psi_i O_j^*\psi_j^*\, d\tau = \overline{O}_{ji}^* \tag{3-A7d}$$

Often we are concerned with quantities where the average value in transition in one direction is the same as the average value in the reverse direction. Sometimes the quantity is independent of the state of the system and is conserved ($O_i = O_j$). For example, O might be a perturbation potential energy that is a function of the coordinates but is externally induced and does not depend on the state of the system acted on by the perturbation. In such cases, the averages $\overline{O}_{ij}$ and $\overline{O}_{ji}$ are equal, and if the observable is everywhere a real quantity the averages must also equal their complex conjugates. Then

$$\int\psi_j^*(\tilde{O}\psi_i)d\tau = \int\psi_i(\tilde{O}^*\psi_j^*)d\tau \tag{3-A8}$$

Equation (3-A8) defines an operator known as Hermitian with respect to the entire class of functions. Note that if O is a constant, such as total energy or total angular momentum, the integrals in equations (3-A7) and (3-A8) all vanish by virtue of the orthogonality relation, equation (3-A5), so that the operator for any constant quantity is automatically Hermitian.

Next consider some specific cases of the general relations above in Cartesian, spherical, and cylindrical coordinate systems. First, the momentum operator of a particle in Cartesian coordinates ($-i\hbar\,\partial/\partial x$) is found to be Hermitian with respect to a given wave function ψ:

$$\overline{p_x} = -i\hbar \int_{-\infty}^{\infty} \psi^* \frac{\partial\psi}{\partial x}\, dx = -i\hbar\left(|\psi^*\psi|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \psi \frac{\partial\psi^*}{\partial x}\, dx \right)$$

$$= i\hbar \int \psi \frac{\partial\psi^*}{\partial x}\, dx = \overline{p_x}^* \qquad \text{(3-A9)}$$

The first integral above has been integrated by parts, with $u = \psi^*$ and $dv = (\partial\psi/\partial x)dx$. The term $|\psi^*\psi|_{-\infty}^{\infty}$ vanishes because the wave function must vanish at the limits $x \to \pm\infty$.

The kinetic energy operator $\widetilde{p_x^2/2m}$ is obtained by successive operations:

$$\frac{\widetilde{p_x^2}}{2m} = -\frac{i\hbar}{2m}\frac{\partial}{\partial x}\left(-i\hbar\frac{\partial}{\partial x}\right) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \qquad \text{(3-A10)}$$

and this operator is also Hermitian.

Problem 3.8: Show that

$$\overline{p_x^{\,2}} = -\hbar^2 \int_{-\infty}^{\infty} \psi^* \frac{\partial^2\psi}{\partial x^2}\, dx = \hbar^2 \int \frac{\partial\psi}{\partial x}\frac{\partial\psi^*}{\partial x}\, dx = \overline{p_x^{\,2}}^* \qquad \text{(3-A11)}$$

Use integration by parts. Note that not only the wave function but also all its derivatives must vanish at the limits $x \to \pm\infty$ if the probability is to be everywhere finite.

In spherical coordinates, the operators are not quite as simple as in Cartesian coordinates. Consider a particle's radial momentum p_r and its conjugate coordinate r, for example. If p_r is replaced by the simple derivative $-i\hbar\, \partial/\partial r$, the resulting operator is not Hermitian because of the r^2 factor that appears in the spherical volume element. However, if the momentum is expressed in an equivalent form

$$p_r = \frac{1}{r}(p_r r) \qquad \text{(3-A12a)}$$

and then the radial momentum is replaced by the derivative $-i\hbar\, \partial/\partial r$:

$$\widetilde{\frac{1}{r}(p_r r)} = \frac{1}{r}\left(-i\hbar\frac{\partial}{\partial r} r\right) = -i\hbar\left(\frac{\partial}{\partial r} + \frac{1}{r}\right) \qquad \text{(3-A12b)}$$

the resulting operator is found to be Hermitian with respect to any spherical wave function ψ that vanishes at the limit $r \to \infty$:

$$\overline{p_r} = -i\hbar\int_0^\infty \psi^* \left(\frac{\partial\psi}{\partial r} + \frac{\psi}{r}\right) r^2\, dr$$

$$= -i\hbar\left(\left|\psi\psi^* r\right|_0^\infty - \int_0^\infty \psi\, \frac{\partial\psi^*}{\partial r}\, r^2\, dr - \int_0^\infty \psi\psi^* r\, dr\right)$$

$$= i\hbar \int_0^\infty \psi \left(\frac{\partial\psi^*}{\partial r} + \frac{\psi^*}{r}\right) r^2\, dr = \overline{p_r}^* \tag{3-A13}$$

Problem 3.9: Show that the operator $-i\hbar(\partial/\partial r)$ is not Hermitian with respect to wave functions expressed in spherical coordinates.

Show that the operator for the kinetic energy associated with the radial momentum of a particle is Hermitian when expressed in the form

$$-\frac{\hbar^2}{2mr}\left(p_r{}^2 r\right) \qquad -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) \tag{3-A14}$$

Show that the operator in equation (3-A14) is obtained by two successive applications of the operator in equation (3-A12b).

In cylindrical coordinates, the situation is slightly more complex yet. The Hermitian operator for the radial momentum of a particle is obtained when the momentum is expressed as the average of two operators:

$$\widetilde{\frac{1}{2}\left(p_r + \frac{1}{r}\, p_r r\right)} = -i\hbar\left(\frac{\partial}{\partial r} + \frac{1}{2r}\right) \tag{3-A15}$$

In this case, however, a Hermitian operator for momentum squared is not obtained when two successive applications of the operator in equation (3-A15) are used.

Problem 3.10: Show that $-\hbar^2[(\partial/\partial r) + (1/2r)][(\partial/\partial r) + (1/2r)]$ does not lead to a Hermitian operator for momentum squared in cylindrical coordinates.

Show that the following average of two operators is Hermitian in cylindrical coordinates:

$$\widetilde{\frac{1}{2}\left(p_r{}^2 + \frac{1}{r}\, p_r{}^2 r\right)} = -\hbar^2\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r}\right) \tag{3-A16}$$

The Hermitian operators in equation (3-A14) and (3-A16) correspond to the usual Laplacian operators in spherical and cylindrical coordinates when the function depends only on r and is independent of the angles. However, particles trapped in a potential well typically have angular momentum as well as radial momentum. The angular momentum operators may or may not be Hermitian, depending on whether the angular momentum is an observable. For example, when the potential is given in spherical coordinates, the wave function may be expressed as a series of terms of the type $P_l{}^m(\cos\,\theta)e^{im\phi}$, where the $P_l{}^m$ are the associated Legendre polynomials. Such wave functions are used for rotating molecules in chapter 4, for example. The operator for azimuthal angular momentum (rotation about the polar axis) is

$$\widetilde{p_\phi} = -i\hbar\,\frac{\partial}{\partial\phi} \tag{3-A17}$$

Using this operator with normalized wave functions of the type $e^{im\phi}/(2\pi)^{1/2}$ one obtains

$$\overline{p_\phi} = -\frac{i\hbar}{2\pi}\int_0^{2\pi} e^{-im\phi}\left(\frac{\partial}{\partial\phi}e^{im\phi}\right)d\phi = m\hbar = \overline{p_\phi}^* \qquad \text{(3-A18)}$$

(Note that m may be either a positive or negative integer.) Thus the operator in equation (3-A17) is Hermitian for this class of functions and represents a real observable. Similarly, the operator for azimuthal angular momentum squared is Hermitian:

$$\overline{p_\phi^{\,2}} = -\frac{\hbar^2}{2\pi}\int_0^{2\pi} e^{-im\phi}\left(\frac{\partial^2}{\partial\phi^2}e^{im\phi}\right)d\phi = m^2\hbar^2 = \overline{p_\phi^{\,2}}^* \qquad \text{(3-A19)}$$

However, the operator for polar angular momentum p_θ (rotations about the origin in a plane of constant ϕ) is not Hermitian when the wave function is a purely real quantity in θ. Let P be any such real function; then the operation on P and integration over all angles yields

$$\overline{p_\theta} = -i\hbar\int_0^{\pi} P\frac{\partial P}{\partial\theta}\sin\theta\, d\theta = -\overline{p_\theta}^* \qquad \text{(3-A20)}$$

The fact that the operator $\widetilde{p_\theta}$ is non Hermitian corresponds to the fact that p_θ is unobservable. Because of the uncertainty principle, once the component of total angular momentum along the polar axis is defined, the direction of the other component is undefinable; this component of momentum may be considered to be precessing about the polar axis (as it would if any slight perturbation were present) and thus having a time average of zero. The magnitude of this component of momentum is definable, however, since the rotational kinetic energy associated with polar angular momentum (i.e., $p_\theta^{\,2}$) is an observable. Accordingly, the operator $\widetilde{p_\theta^{\,2}}$ is found to be Hermitian:

$$\overline{p_\theta^{\,2}} = -\hbar^2\int_0^{\pi} P\frac{\partial^2 P}{\partial\theta^2}\sin\theta\, d\theta = \overline{p_\theta^{\,2}}^* \qquad \text{(3-A21)}$$

In cylindrical symmetry, the angular momentum and the angular momentum squared are given by the same operators used in equations (3-A18) and (3-A19), respectively, while the z component of linear momentum and its square are given by the same operators used for the z axis components in Cartesian coordinates.

With this review of the operators involved, consider the character of the spherically symmetric wave function:

$$\psi = \frac{e^{ikr}}{r} \qquad \text{(3-A22)}$$

which satisfies the Schroedinger equation in spherical coordinates for a wave function independent of θ and ϕ:

$$\frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r} = -k^2\psi \qquad \text{(3-A23)}$$

In this equation, k^2 is the energy E in units of $\hbar^2/2ma_o^2$ and r is in units of a_o.

If we operate on the function in equation (3-A22) with the radial momentum operator and then divide by the wave function,

$$p_r = -\frac{i\hbar\left(\frac{\partial}{\partial r} + \frac{1}{r}\right)\left(\frac{e^{ikr}}{r}\right)}{\frac{e^{ikr}}{r}} = k\hbar \qquad \text{(3-A24)}$$

Thus, the wave function in equation (3-A22) represents a spherically uniform wave front that describes a particle with radial momentum $k\hbar$. If k is positive the wave advances outward; if negative, the wave advances inward. Standing waves in a potential well are composed of outward- and inward-traveling waves and the wave functions are superpositions of functions with both positive and negative values of k. If the potential V is some arbitrary function of r, the steady-state or standing wave function has the character of a series of such functions:

$$\psi \sim \frac{C}{r}\left\{e^{i[2m(E-V)]^{1/2}r/\hbar} \pm e^{-i[2m(E-V)]^{1/2}r/\hbar}\right\} \qquad \text{(3-A25)}$$

in the region $E > V$, and decreases exponentially in the region $V > E$:

$$\psi \sim \frac{C}{r}\, e^{-[2m(V-E)]^{1/2}r/\hbar} \qquad \text{(3-A26)}$$

For a stepped approximation to the potential V, the standing wave function is a sequence of wave functions of the above type which matches magnitudes and first derivatives at the interfaces. The spherically symmetric standing waves thus have the characteristics of $C \cos kr/r$ or $C \sin kr/r$, with variable wave number k and amplitude C, similar to the plane wave functions discussed in section 3.3 except for the factor r^{-1}. This factor is just that required to conserve the probability flux of a spherically uniform wave growing in its cross-sectional area as r^2.

The wave function of a cylindrically symmetric wave is somewhat more involved near the origin where solutions to the Schroedinger equation are Bessel functions; but, at large values of r, these solutions reduce to the form

$$\lim_{r\to\infty} \psi = \frac{e^{ikr}}{r^{1/2}} \qquad \text{(3-A27)}$$

Once again, the wave function corresponds to an outgoing wave if k is positive. Standing wave functions have the character $C \cos kr/r^{1/2}$ and $C \sin kr/r^{1/2}$ in the region $E > V$ and fall off exponentially as $C\, e^{-kr}/r^{1/2}$ in the region $V > E$.

With the above general characteristics of plane waves, spherically symmetric waves, and cylindrically symmetric waves in mind, one can more readily visualize wave functions and their properties in cases of rather arbitrary symmetry, and also visualize the physical meaning of Hermitian operators for momentum and momentum squared.

Problem 3.11: Show that a solution to the Schroedinger equation in cylindrical coordinates for a wave function independent of ϕ and z

$$\frac{\partial^2\psi}{\partial r^2} + \frac{1}{r}\frac{\partial\psi}{\partial r} = -k^2\psi \tag{3-A28}$$

can be expressed as

$$\psi = \frac{e^{ikr}}{r^{1/2}} \sum_{n=0}^{\infty} \frac{a_n}{r^n} \tag{3-A29}$$

where the coefficients a_n are given by

$$a_{n+1} = \frac{(-i)^{n+1}}{(8k)^{n+1}(n+1)!}\left[\frac{(2n+1)!}{2^n n!}\right]^2 a_o \tag{3-A30}$$

For large r, find that this series asymptomatically approaches

$$\psi \to \frac{e^{ikr}}{r^{1/2}} = \frac{\cos kr}{r^{1/2}} + i\,\frac{\sin kr}{r^{1/2}} \tag{3-A31a}$$

which, except for a normalizing constant, is proportional to Bessel functions of half integer order:

$$\psi \to J_{-1/2}(kr) + iJ_{1/2}(kr) \tag{3-A31b}$$

Problem 3.12: Show that the wave function given by equation (3-A31a) **represents a cylindrically uniform wave** front with outgoing momentum $k\hbar$. Use the momentum operator in equation (3-A15):

$$p_r = -\frac{i\hbar}{e^{ikr}/r^{1/2}}\left(\frac{\partial}{\partial r} + \frac{1}{2r}\right)\left(\frac{e^{ikr}}{r^{1/2}}\right) = k\hbar \tag{3-A32}$$

C-2

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CHAPTER 4 - RIGID ROTATORS

4.1 SUMMARY

The two-particle, steady-state Schroedinger equation is transformed to center of mass and internuclear distance vector coordinates, leading to the free particle wave equation for the kinetic energy motion of the molecule and a decoupled wave equation for a single particle of reduced mass moving in a spherical potential field. The latter describes the vibrational and rotational energy modes of the diatomic molecule. For fixed internuclear distance, this becomes the equation of rigid rotator motion. The classical partition function for the rotator is derived and compared with the quantum expression. Molecular symmetry effects are developed from the generalized Pauli principle that the steady-state wave function of any system of fundamental particles must be antisymmetric. Nuclear spin and spin quantum functions are introduced and ortho- and para-states of rotators, along with their degeneracies, are defined. Effects of nuclear spin on entropy are deduced. Next, rigid polyatomic rotators are considered and the partition function for this case is derived. The patterns of rotational energy levels for nonlinear molecules are discussed for the spherical symmetric top, for the prolate symmetric top, for the oblate symmetric top, and for the asymmetric top. Finally, the equilibrium energy and specific heat of rigid rotators are derived.

4.2 INTRODUCTION

The diatomic molecule behaves as though it consists of two mass centers connected by a rather stiff spring. Following a collision between two molecules in a gas, the centers of mass of the colliding particles fly apart. At the same time, the molecules are usually rotating about their centers of mass, and if the previous collisions have been energetic enough to compress the stiff spring, the atomic centers of the molecule will also be in vibrational motion along the distance vector between them. Polyatomic molecules behave in a similar manner, generally rotating about their center of mass as an asymmetric top and vibrating as a collection of mass points connected by a complex network of springs. In this chapter, the springs or interatomic bonds are considered to be rigid, and the time-independent energy states associated with the purely rotational motions of the molecule are derived.

The moments of inertia of most molecules are large enough that the energy levels of rotational motion are rather close together compared with a typical thermal energy kT. One can thus expect that a classical model of a rigid rotator will duplicate many features of real rotating molecules reasonably well. Nevertheless, quantum effects are clearly present in the pattern of rotational energy levels observed and in the effects of symmetry and nuclear spin that occur. The solutions for molecular rotations obtained with Schroedinger's wave equation are just as simple as the classical solutions, so in this case there is no particular advantage gained by use of the classical model, while much of the exact detail would be lost. Therefore, the subject is approached primarily from the quantum viewpoint.

4.3 SEPARATION OF TRANSLATIONAL AND INTERNAL MODE WAVE FUNCTIONS

Diatomic molecules in steady state, free of external perturbations, obey the two-particle wave equation:

$$\frac{\hbar^2}{2m_1}\nabla_1{}^2\psi + \frac{\hbar^2}{2m_2}\nabla_2{}^2\psi - V(\vec{r}_1 - \vec{r}_2)\psi + E\psi = 0 \tag{4.1}$$

where m_1 and m_2 are the masses of the atoms in the molecule, $V(\vec{r}_1 - \vec{r}_2)$ is the potential between the two atoms expressed as a function of the distance between them, ψ is the total wave function, E is the total energy, and the kinetic energy operator for the *ith* atom is

$$\frac{\hbar^2}{2m_i}\nabla_i{}^2 = \frac{\hbar^2}{2m_i}\left(\frac{\partial^2}{\partial x_i{}^2} + \frac{\partial^2}{\partial y_i{}^2} + \frac{\partial^2}{\partial z_i{}^2}\right) \tag{4.2}$$

Equation (4.1) is transformed from the coordinate system described by $\vec{r}_1$ and $\vec{r}_2$, the vector position of the two atoms, to the center-of-mass coordinate vector $\vec{R}$ and the radius vector $\vec{r}$ between the two atoms with the following relations:

$$\vec{r} = \vec{r}_1 - \vec{r}_2 \tag{4.3}$$

$$\vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2} \tag{4.4}$$

which have the x components:

$$x = x_1 - x_2 \tag{4.3a}$$

$$X = \frac{m_1}{m_1 + m_2}x_1 + \frac{m_2}{m_1 + m_2}x_2 \tag{4.4a}$$

and similar expressions for the y and z components. The partial derivative operators become

$$\frac{\partial^2}{\partial x_1{}^2} = \frac{\partial^2}{\partial x^2} + \frac{2m_1}{m_1 + m_2}\frac{\partial^2}{\partial x\,\partial X} + \left(\frac{m_1}{m_1 + m_2}\right)^2\frac{\partial^2}{\partial X^2} \tag{4.5}$$

$$\frac{\partial^2}{\partial x_2{}^2} = \frac{\partial^2}{\partial x^2} - \frac{2m_2}{m_1 + m_2} \frac{\partial^2}{\partial x \, \partial X} + \left(\frac{m_2}{m_1 + m_2}\right)^2 \frac{\partial^2}{\partial X^2} \tag{4.6}$$

again with similar expressions for derivatives with respect to y and z. The sum of the first two terms in equation (4.1) thus include terms such as

$$\frac{1}{m_1} \frac{\partial^2}{\partial x_1{}^2} + \frac{1}{m_2} \frac{\partial^2}{\partial x_2{}^2} = \left(\frac{1}{m_1} + \frac{1}{m_2}\right) \frac{\partial^2}{\partial x^2} + \frac{1}{m_1 + m_2} \frac{\partial^2}{\partial X^2} \tag{4.7}$$

and the two-particle wave equation can be expressed as

$$\frac{\hbar^2}{2M} \nabla_R{}^2 \psi + \frac{\hbar^2}{2\mu} \nabla_r{}^2 \psi - V(r)\psi + E\psi = 0 \tag{4.8}$$

where M is the total mass, $m_1 + m_2$, and μ is the reduced mass defined by

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \tag{4.9}$$

Assume the wave function is separable:

$$\psi(R,r) = f(R)g(r) \tag{4.10}$$

Then the wave equation can be written as

$$\frac{1}{f} \frac{\hbar^2}{2M} \nabla_R{}^2 f + \frac{1}{g}\left(\frac{\hbar^2}{2\mu} \nabla_r{}^2 g - Vg\right) + E = 0 \tag{4.11}$$

The first term on the left is a function only of the center-of-mass coordinate R, the second term only of the distance between atoms r. If the sum of these two functions is to be the constant ($-E$) for arbitrary values of R and r, then the individual terms must be constants. These constants are designated the translational energy of the center of mass, E_t, and the internal energy of the molecule, E_i. Thus, the center of mass obeys the free-particle wave equation:

$$\frac{\hbar^2}{2M} \nabla_R{}^2 f + E_t f = 0 \tag{4.12}$$

while the internal motions are described by

$$\frac{\hbar^2}{2\mu} \nabla_r{}^2 g + [E_i - V(r)]g = 0 \tag{4.13}$$

a wave equation with the same form as one that describes a single particle with mass μ moving in the potential field $V(r)$.

The wave equations given above apply not only to the bound state of two atoms in a diatomic molecule, but also to the collision process between any two free particles. Collision processes are not of primary concern here since the same equilibrium state results regardless of the path followed toward equilibrium. However, the engineer is ultimately interested in nonequilibrium properties as well, such as viscosity, thermal conductivity, mass diffusion, electrical conductivity, etc., and these properties are uniquely determined by two-body collision processes in gases of normal density. Thus it may be appropriate to point out that the separation of the wave equation into equations (4.12) and (4.13) immediately tells us something about conserved quantities in any collision process: The kinetic energy, E_t, associated with the total mass moving with the center-of-mass velocity is a conserved quantity in collision, and is thus unavailable for excitation of internal energy of the colliding particles. The only energy available for this purpose is the kinetic energy E_i associated with the reduced mass μ moving with the velocity of relative motion between the particles. In the free state, this energy can be described as the sum of a component associated with just the change in distance between particles, and a component associated with the angular momentum of the particles about their centers of mass. In the bound state, E_i is the sum of the vibrational and rotational energy of the diatomic molecule.

Problem 4.1: Show that the wave equation for three particles with masses m_1, m_2, and m_3 can be expressed as

$$\frac{\hbar^2}{2M}\nabla_R{}^2\psi + \frac{\hbar^2}{2\mu'}\nabla_{r'}^{2}\psi + \frac{\hbar^2}{2\mu}\nabla_r{}^2\psi - V\psi = E\psi$$

where M is the total mass,

$$M = m_1 + m_2 + m_3$$

The term μ' is another reduced mass given by

$$\frac{1}{\mu'} = \frac{1}{m_3} + \frac{1}{m_1 + m_2}$$

and μ is the reduced mass in equation (4.9).

The center-of-mass coordinate $\vec{R}$ is, in this case,

$$\vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2 + m_3\vec{r}_3}{M}$$

while r is the distance between atoms 1 and 2 as given in equation (4.3) and r' is the distance between atom 3 and the center of mass of atoms 1 and 2:

$$\vec{r}' = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2} - \vec{r}_3$$

Further show that if the potential can be expressed as a linear superposition of functions of r and of r',

$$V = V(r) + V'(r')$$

the steady-state wave function can then be expressed as a product of separable functions:

$$\psi(R,r,r') = f(R)g(r)h(r')$$

Show that this leads to a wave equation for a free particle with mass M, a wave equation for a particle with mass μ moving in the potential field $V(r)$, and a wave equation for a particle with mass μ' moving in the potential field $V'(r')$, each with a constant component of energy. Note that this process can be repeated with the addition of still more particles, and so long as the potential is independent of the center-of-mass coordinate,

$$\vec{R} = \frac{\sum_i m_i\vec{r}_i}{\sum_i m_i}$$

a wave equation for a free particle with total mass $\sum_i m_i$ results that describes the motion of the center of mass of the system. Thus, in any system of interacting particles, the kinetic energy associated with the center-of-mass motion is a conserved quantity and is unavailable for chemical reaction or excitation of internal energy.

4.4 CLASSICAL RIGID ROTATORS

The classical rigid-rotator model of a diatomic molecule consists of two mass points constrained to be a fixed distance r_o apart (fig. 4.1). The model is free to rotate about the center of mass, and the angular momentum is represented by a vector $\vec{L}$ orthogonal to the molecular axis with the magnitude $\mu r_o^2\omega$, where μ is the reduced mass and ω is the angular velocity. Classically, this rotator possesses the energy

$$E = \frac{\mu r_o^2\omega^2}{2} = \frac{L^2}{2I} \tag{4.14}$$

where I is the moment of inertia, μr_o^2.

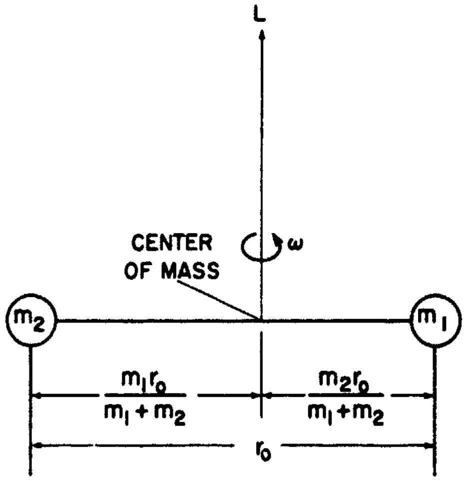


Figure 4.1.- Rigid diatomic rotator with angular momentum $L = \frac{m_1 m_2}{m_1 + m_2} r_o^2\omega$.

Problem 4.2: Verify that the total kinetic energy of two point masses m_1 and m_2, fixed a distance r_o apart and rotating about their center of mass with angular velocity ω, is the same as the kinetic energy of a single particle of mass $\mu = m_1m_2/(m_1 + m_2)$, which is constrained to move along a circle of radius r_o with the same angular velocity ω.

The angular momentum involves two independent momentum coordinates, and it may be decomposed into two mutually orthogonal components:

$$L^2 = L_1^2 + L_2^2 \tag{4.15}$$

(A third spatially orthogonal vector component is eliminated as an independent variable by the relation that L is orthogonal to the molecular axis.) We shall choose a spherical coordinate system with the polar axis lying in the plane defined by $\vec{L}$ and $\vec{r}_o$ at the polar angle θ with respect to $\vec{r}_o$ (fig. 4.2).

Problem 4.3: Show that the element of phase space $dp_1\, dp_2\, dq_1\, dq_2$ for the particle shown in figure 4.2 (where p_1 and p_2 are orthogonal components of the linear momentum vector $\vec{p}$, and q_1 and q_2 are corresponding distance coordinates) can be expressed in terms of the angular momentum components L_θ and L_ϕ and the angles θ and ϕ

$$dp_1\, dp_2\, dq_1\, dq_2 = dp_\theta\, dp_\phi\, dq_\theta\, dq_\phi = dL_\theta\, dL_\phi\, \sin\theta\, d\theta\, d\phi \tag{4.16}$$

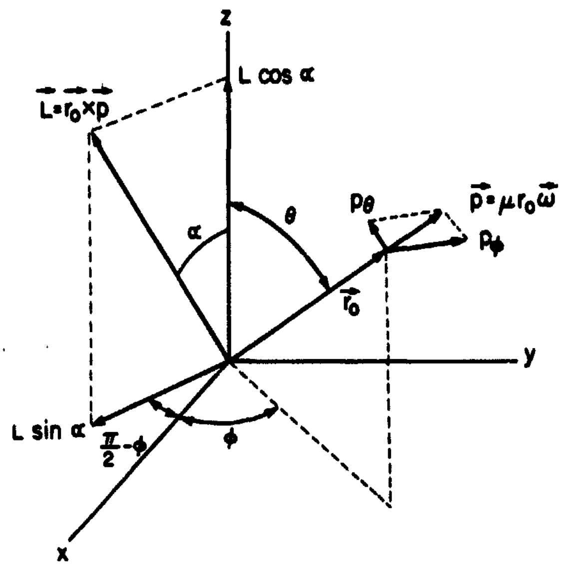


Figure 4.2.- Coordinate system, angular momentum $\vec{L}$, and linear momentum $\vec{p}$ for the rigid diatomic rotator's equivalent single-particle motion. The effective mass is the reduced mass μ, the radius vector $\vec{r}_0$ is constant in magnitude, and the linear momentum $\vec{p}$ is orthogonal to $\vec{r}_0$.

With the relation given by equation (4.16), the classical partition function (see eq. (1.52b)) for the rigid rotator is written:

$$Q_r = \frac{1}{h^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{0}^{\pi}\int_{0}^{2\pi} e^{-(L_\theta+L_\phi)^2/2IkT}\, dL_\theta\, dL_\phi\, \mathit{ein}\,\theta\, d\theta\, d\phi \tag{4.17}$$

The integrations over θ and ϕ give the total solid angle, 4π steradians, and equation (4.17) becomes

$$Q_r = \frac{4\pi}{h^2}\left(\int_{-\infty}^{\infty} e^{-L_i^2/2IkT}\, dL_i\right)^2 = \frac{8\pi^2 IkT}{h^2} = \frac{T}{\theta_r} \tag{4.18}$$

where θ_r is a characteristic rotational temperature $\hbar^2/2Ik$.

The unit of angular momentum in classical phase space may be deduced from the uncertainty principle developed in chapter 3:

$$\Delta p_i\ \Delta q_i = h \tag{4.19}$$

where p_i and q_i represent a linear momentum and its conjugate distance coordinate, respectively. For a particle moving in a circle of radius r_o, the maximum uncertainty in linear position is

$$\Delta q = 2\pi r_o \tag{4.20}$$

which corresponds to the minimum uncertainty in angular momentum

$$\Delta l = r_o\ \Delta p \tag{4.21}$$

Thus Δl is

$$\Delta l = r_o\,\frac{h}{\Delta q} = \frac{h}{2\pi} = \hbar \tag{4.22}$$

the quantum unit of angular momentum. The angular momentum can thus be determined only within some interval that is a multiple of $\hbar$:

$$L = \hbar l \tag{4.23}$$

where l is an integer. The classical energy of a two-dimensional rigid rotator expressed in these units is

$$E = \frac{\hbar^2 l^2}{2I} = k\theta_r l^2 \tag{4.24}$$

Problem 4.4: Show that, for two independent modes of angular momentum, the number of cells of phase space which have the total energy given by equation (4.24) is $2l$. Using this value for the degeneracy, $g(l)$, show that the phase integral expressed in the form

$$Q_r = \frac{1}{\hbar^2}\int_{-\infty}^{\infty} g(l)e^{-E(l)/kT}\,dl \tag{4.25}$$

leads to the same results as equation (4.18).

4.5 QUANTIZED RIGID ROTATORS

The rigid rotator has only kinetic energy; the potential is zero so the steady-state wave equation is

$$\nabla^2 Y + \frac{2\mu}{\hbar^2} EY = 0 \tag{4.26}$$

The wave function Y is separable in spherical angular coordinates θ and ϕ:

$$Y(\theta,\phi) = P(\theta)\Phi(\phi) \tag{4.27}$$

Substituting equation (4.27) into (4.26) and dividing by Y one obtains

$$\frac{1}{\Phi r_o^2 \sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2} + \frac{1}{Pr_o^2 \sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right) + \frac{2\mu}{\hbar^2}E = 0 \tag{4.28}$$

which can be arranged as a sum of separate functions of θ and of ϕ

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} + \left[\frac{\sin\theta}{P}\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right) + \frac{2IE}{\hbar^2}\sin^2\theta\right] = 0 \tag{4.29}$$

The two terms on the left must be constants, one the negative of the other, to satisfy this relation for arbitrary choice of θ and ϕ. Let

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2 \tag{4.30}$$

For which a solution is

$$\Phi(\phi) = \frac{e^{\pm im\phi}}{\sqrt{2\pi}} \tag{4.31}$$

The term m must be integer for Φ to be single valued, and the constant of integration $(2\pi)^{-1/2}$ has been normalized so there is unit probability that the rotator appears somewhere in the interval $0 < \phi < 2\pi$, that is, the integral of $\Phi\Phi^*$ over all ϕ is unity.

The remaining equation for P now becomes

$$\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{dP}{d\theta}\right) + \left(\frac{2IE}{\hbar^2}\sin^2\theta - m^2\right)P = 0 \tag{4.32}$$

which is the Legendre differential equation. A finite solution exists only for energy values given by

$$E = \frac{\hbar^2}{2I}\, l(l + 1) = l(l + 1)k\theta_r \tag{4.33}$$

with l constrained to integer values equal to or greater than m, that is, $l \geq m$. Conversely, the values of m are constrained to integer values between zero and l, that is, $0 \leq m \leq l$. The solutions, $P = P_l^m(\cos\theta)$ are power series with a finite number of terms known as the associated Legendre polynomials. The allowed steady-state energy levels for the quantized rotator differ from the classical rotator in that $l(l + 1)$ replaces l^2 in equation (4.24). The difference becomes small at large values of l, an example of the correspondence prinicple. Since the quantized total angular momentum is $\hbar\sqrt{l(l + 1)}$, the classical relation between energy and angular momentum is retained.

Solutions to equation (4.32) in terms of the associated Legendre polynomials are derived in any elementary text on quantum mechanics (refs. 1 and 2) and are not repeated here. The total rotational wave function is the spherical harmonic function:

$$Y_l^{\pm m}(\theta,\phi) = \frac{e^{\pm im\phi}}{\sqrt{2\pi}} \sqrt{\frac{(2l + 1)(l - m)!}{2(l + m)!}}\, P_l^m(\cos\theta) \tag{4.34}$$

where the factor $[(2l + 1)(l - m)!/2(l + m)!]^{1/2}$ is the normalizing constant required so that integration of YY^* over all 4π steradians is unity. Note that m is defined as a positive integer here, and both positive and negative values are allowed by including both positive and negative exponentials in the solutions for $\Phi(\phi)$ (eq. (4.31)). Often m is treated as a positive or negative integer; then the absolute values must be specified in the associated Legendre function and its normalizing constant.

The first few associated Legendre polynomials are

$$\left.\begin{aligned}
P_0^{\,0} &= 1\\
P_1^{\,0} &= x = \cos\theta\\
P_1^{\,1} &= (1 - x^2)^{1/2} = \sin\theta\\
P_2^{\,0} &= \frac{1}{2}(3x^2 - 1) = \frac{1}{2}(3\cos^2\theta - 1)\\
P_2^{\,1} &= 3x(1 - x^2)^{1/2} = 3\cos\theta\sin\theta\\
P_2^{\,2} &= 3(1 - x^2) = 3\sin^2\theta\\
P_3^{\,0} &= \frac{1}{2}(5x^3 - 3x) = \frac{1}{2}(5\cos^3\theta - 3\cos\theta)\\
P_3^{\,1} &= \frac{1}{2}(15x^2 - 3)(1 - x^2)^{1/2} = \frac{3}{2}(5\cos^2\theta - 1)\sin\theta\\
P_3^{\,2} &= 15x(1 - x^2) = 15\sin^2\theta\cos\theta\\
P_3^{\,3} &= 15(1 - x^2)^{3/2} = 15\sin^3\theta\\
P_4^{\,0} &= \frac{35}{8}x^4 - \frac{15}{4}x^2 + \frac{3}{8} = \frac{35}{8}\cos^4\theta - \frac{15}{4}\cos^2\theta + \frac{3}{8}
\end{aligned}\right\} \tag{4.35}$$

Additional members can be derived from the recursion relations:

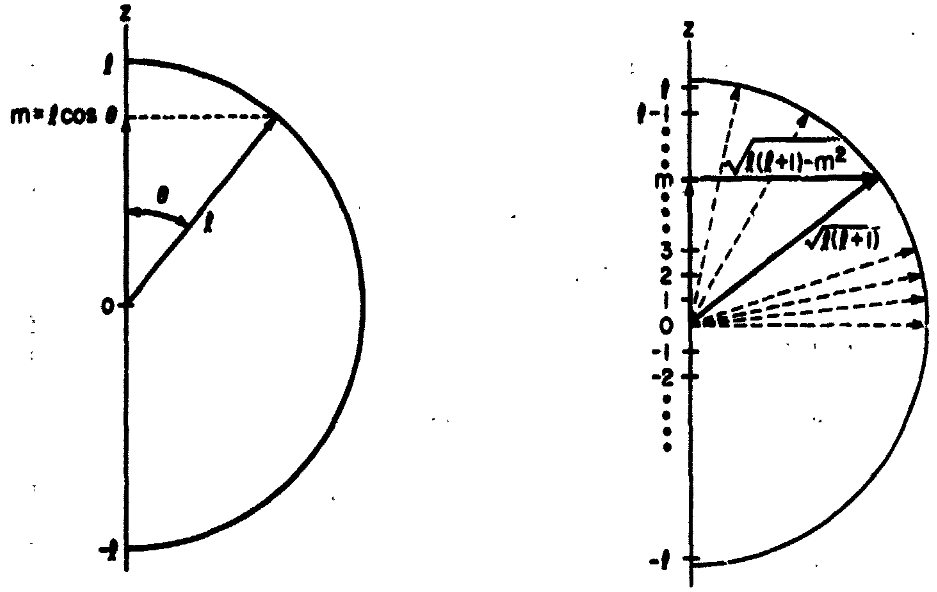
$$(l - m + 1)P_{l+1}^{m} = (2l + 1)xP_l^m - (l + m)P_{l-1}^{m} \tag{4.36a}$$

$$(2l + 1)(1 - x^2)^{1/2}P_l^{m+1} = (l + m)(l + m + 1)P_{l-1}^{m} - (l - m)(l - m + 1)P_{l+1}^{m} \tag{4.36b}$$

or from the relation between Legendre polynomials P_l^0 and the associated Legendre polynomials P_l^m:

$$P_l^m(x) = (1 - x^2)^{m/2}\,\frac{d^mP_l^0(x)}{dx^m} \tag{4.36c}$$

The quantum number m represents the magnitude of the projection of the total angular momentum (in units of $\hbar$) on the polar axis of the coordinate system chosen. Classically, the total angular momentum is l and its projection on the polar axis, $l\cos\theta$, may take any value from $-l$ to l (fig. 4.3a). For the quantized rotator, the total angular momentum is $\sqrt{l(l + 1)}$ units of $\hbar$ and its projection on the polar axis can take the $(2l + 1)$ integer values from $-l$ to l including zero (fig. 4.3(b)). In other words, the degeneracy of states with total angular momentum $\sqrt{l(l + 1)}\hbar$ and rotational energy $l(l + 1)k\theta_r$ is $(2l + 1)$.



(a) Classical rotator's total angular momentum vector l (in units of $\hbar$) may be at angle θ and have the projection $m = l \cos\theta$ on the polar axis, which takes any value from l to $-l$. Without an external field, the vector l remains fixed in space. If the angular momentum is coupled to a field aligned with the polar axis, the component m remains fixed while the component $l \sin\theta$ precesses about the polar axis with an angular velocity that increases with the strength of the coupling.

(b) Quantized rotator's total angular momentum vector $\sqrt{l(l+1)}$ (in units of $\hbar$) takes one of the $(2l + 1)$ possible positions with respect to the polar axis, for which the projection m is any integer from l to $-l$. Again, the total angular momentum vector remains fixed in space without an external field, but if coupled to a field aligned with the polar axis the component m remains fixed while the component $[\sqrt{l(l+1)-m^2}]$ precesses about the axis.

Figure 4.3.- Rotator angular momentum and its projections on an axis of symmetry.

The quantum partition function for a diatomic rotator is thus

$$Q_r = \sum_{l=0}^{\infty} (2l + 1)e^{-l(l+1)\theta_r/T} \qquad (4.37a)$$

In the limit as T becomes large compared with θ_r, the summation can be approximated by the integral

$$Q_r \xrightarrow[T \gg \theta_r]{} \int_0^{\infty} (2l + 1)e^{-l(l+1)\theta_r/T}\, dl = \frac{T}{\theta_r} \qquad (4.37b)$$

which gives the same result as the classical model. At lower temperatures, the summation in equation (4.37a) should be performed for the first few terms, then the remaining series can be approximated with an integral

$$Q_r \approx \sum_{l=0}^{n} (2l + 1)e^{-l(l+1)\theta_r/T} + \frac{T}{\theta_r} e^{-n(n+1)\theta_r/T} \tag{4.37c}$$

At very high temperatures, the rigid-rotator partition function is proportional to T without limit, as given by equation (4.37b). This behavior is due to the infinite number of energy levels that exist for the rigid rotator. A qualitatively more realistic model of real molecules would truncate the rigid-rotator levels at the dissociation limit D, in which case the maximum rotational quantum number l' is approximately given by

$$l'(l' + 1) \approx \frac{D}{k\theta} \tag{4.33a}$$

The integral approximation to the partition function sum then approaches a finite limit:

$$\int_0^{l'} (2l + 1)e^{-l(l+1)\theta/T}\, dl = \frac{T}{\theta}\left(1 - e^{-D/kT}\right) \xrightarrow[T>>D/k]{} \frac{D}{k\theta} \tag{4.37d}$$

This limit is large - the order of 10^4 for many diatomic molecules.

In practice, a correction for truncation of the rotational energy levels is normally unnecessary. Corrections for centrifugal stretching and vibration-rotation coupling (considered later) are far larger at temperatures of interest. Molecules are normally all dissociated at temperatures the order of D/k, where the asymptotic limit on rotational partition must be considered. However, the truncated-rotator model does illustrate the qualitative concept that a finite limit to the partition function does exist.

In spectroscopic notation, the observed rotational energy levels are expressed as

$$E_r = BJ(J + 1) \tag{4.38}$$

where J replaces the rotational quantum number l, and B is the rotational energy constant. The rotational constants are usually listed in wave numbers; the energy is then in units of hc. The constant B in wave numbers is related to the moment of inertia I and the characteristic temperature θ_r by

$$B = \frac{\hbar}{4\pi cI} = \frac{k\theta_r}{hc} \tag{4.39}$$

A few typical values of B and θ_r for diatomic molecules are given in table 4.1. Except for H_2 and D_2, the values of θ_r are well below the critical temperature where gas phase cannot exist. Since the classical

TABLE 4.1.- ROTATIONAL CONSTANTS FOR DIATOMIC MOLECULES[a]

Molecule or radical	B, cm^{-1}	θ_r, °K	r_o, Å
H_2	59.37	85.42	0.7506
HD	44.15	63.52	.7539
D_2	29.93	43.06	.7477
O_2	1.4378	2.069	1.2107
N_2	2.001	2.879	1.0968
NO	1.6957	2.440	1.1538
CO	1.9227	2.766	1.1308
Cl_2	0.2430	0.3496	1.9918
Br_2	.08077	.1162	2.2856
I_2	.03730	.0537	2.6687
OH	18.514	26.64	0.9799
CH	14.190	20.42	1.1303
HCl	10.440	15.02	1.2838
HBr	8.360	12.03	1.4233

[a] Molecules are assumed to be composed of the most common atomic isotopes and the constants given obtain for the ground vibrational state (i.e., B_o and r_o in spectroscopic notation), since these are appropriate to the calculation of the partition function where energies are measured relative to the ground state. The spectroscopic values B_e and r_e which obtain at the potential minimums are slightly different due to rotation-vibration coupling as discussed in Chapter 8. $B_o = B_e - \alpha_e/2$, where α_e is the rotation-vibration coupling constant.

approximations for rotational partition function are adequate whenever $T >> \theta_r$, the more exact quantum solutions must be considered for gas phase only for H_2 and D_2. Even then, the classical approximation is adequate at normal temperatures and above. The interatomic distance $r_o = (I/\mu)^{1/2}$ is also listed. Note that the values of r_o are all the order of 1 Å. This is a consequence of the fact that outer electron orbitals are about the same size for all atoms, so the binding electron interactions occur at about the same internuclear distance.

4.6 MOLECULAR SYMMETRY EFFECTS

One additional factor must be included in the partition function, the symmetry number σ, which equals unity for diatomic molecules when the two atoms in the molecule are different (as with NO, CO, HD, or $O^{16}\,O^{17}$, e.g.) and equals two when the particles are indistinguishable (as with $N^{14}\,N^{14}$ or $O^{16}\,O^{16}$, e.g.). The complete rotational partition function is, in the limit $T >> \theta_r$,

$$Q_r = \frac{T}{\sigma\theta_r} \tag{4.40}$$

Classically, we say the symmetry number occurs because the same observable state occurs when the angle of a homonuclear diatomic rotator changes by π, whereas the angle must change by 2π for the heteronuclear diatomic rotator to arrive at the same observable state. Thus, half the angular range must be excluded from the phase integral for the homonuclear molecule.

In quantum mechanics, we find from the Pauli exclusion principle (discussed in the next section) that the wave function of any system of particles must be antiasymmetric with respect to the exchange of any two fundamental particles - that is, the wave function must change sign when two such particles exchange quantum states. Note that exchanging quantum state involves exchanging position as well as exchanging energy level since the uncertainty principle divides momentum-coordinate space into cells of different quantum state. Thus the rotation of a homonuclear diatomic molecule through the angle π exchanges two like nuclei composed of fundamental particles - protons and neutrons. These nuclei possess both spin and orbital momentum. For a spin state of given symmetry, the orbital momentum must have a given symmetry in accord with the Pauli principle; even orbital symmetry corresponds to even-numbered l integers and odd orbital symemtry corresponds to odd l integers (note the symmetry of the associated Legendre polynomials listed in eq. (4.35)). Thus only half the rotational states are available to a homonuclear diatomic molecule in a given spin state. Even and odd rotational states of such molecules are thus like two separate species, and the partition function for each species includes a summation over half the total number of rotational levels.

The reader is aware that collisions of molecules with other gas particles, with photons, or with the walls of a containing vessel can produce perturbations that change the quantum state of the molecule. These perturbations have a negligible effect on nuclear spin states of the molecule, however, because spin is influenced mainly by magnetic forces that are relatively weak compared with the electrostatic forces that perturb molecules during collision and also because the different spin states are widely separated in energy, with the result that collision perturbations are unlikely to cause transitions in spin state. Thus once a homonuclear diatomic molecule finds itself in a rotational state of one symmetry, it will maintain that symmetry for most practical purposes. Rotational states with even-numbered l will make transitions only to other states with even-numbered l, states with odd-numbered l only to other states with odd-numbered l. Of course, eventually some rare collision event or photon absorption will produce an excited state in which both nuclear spin and rotational symmetries change, leaving the molecule in a new steady state that satisfies the Pauli principle. Thus a mechanism exists for eventually establishing complete equilibrium between even and odd rotational states. However, these events may be so rare that the homonuclear diatomic gas is frozen, for most practical purposes, in whatever nonequilibrium ratio between even and odd states which may be imposed as an initial condition.

To understand the effects of nuclear symmetry in a more fundamental way, the Pauli principle of quantum mechanics and the effects of nuclear spin are considered in more detail in the following sections.

4.7 THE PAULI PRINCIPLE

To state the Pauli principle, the definition of a fundamental particle should first be treated in more detail. A fundamental particle is defined to be an indivisible atomic particle with exactly 1/2 quantum unit of internal angular momentum (called a unit of spin). These may include neutrinos and mesons, for example, but for present purposes, we consider only three fundamental particles: electrons, protons, and neutrons. Atomic nuclei are considered as aggregates of protons and neutrons; molecules consist of a group of such nuclei bound in an electrostatic potential-well resulting from their own charges and the charges of an appropriate number of orbiting electrons. Any particle with more or less that one spin unit is automatically a complex particle; a particle with one spin unit may be a fundamental particle, or a complex particle composed of an odd number of fundamental particles in which all spins are paired except one. Spin states are considered in more detail in section 4.8; for the present, we note that just two spin states are observed, which result in zero spin when paired. Accordingly, particles composed of an even number of fundamental particles must have an even integer number of spin momentum units - such particles are called bosons. Particles composed of an odd number of fundamental particles must have an odd number of spin momentum units - such particles are called fermions. Of course, the fundamental particles themselves are fermions also.

With this introduction to the definition of fundamental particles, the Pauli principle may be stated simply: *no two identical fundamental particles can exist in the same quantum state*. The principle is merely an empirical statement that generalizes all presently known observed facts; it is not derivable from more fundamental principles as far as we know.

A somewhat more general statement of the Pauli principle, which calls attention to the mathematical symmetry relations implied in the elementary statement above, is useful: *generalized Pauli principle - the steady-state wave function of any system of fundamental particles must be antisymmetric.* Recall that antisymmetry means a change in sign of the wave function when any two fundamental particles are interchanged. The value of $\psi\psi^*$, or the probability, is unchanged by this operation, of course. Sometimes the Pauli principle is stated in a slightly different but completely equivalent way: *the steady-state wave function of any system of particles must be antisymmetric with respect to the exchange of any two identical fermions and symmetric with respect to the exchange of any two identical bosons*. The reader can readily see that this statement of the principle follows from the generalized statement given above and from the definitions of fundamental particles, fermions, and bosons. The elementary statement of the principle is also seen to apply as follows:

Consider two *independent* identical particles 1 and 2, with quantum states having the wave functions u_1 and u_2 available to them. A total wave function for the system of two particles can be constructed:

$$\psi(1,2) = u_1(1)u_2(2) \tag{4.41}$$

which describes particle 1 in state u_1 and particle 2 in state u_2. However, this function does not satisfy the generalized Pauli principle because generally when the particles are interchanged,

$$u_1(1)u_2(2) \neq -u_1(2)u_2(1)$$

However, an antisymmetric wave function that satisfies the Pauli principle is

$$\psi_a(1,2) = u_1(1)u_2(2) - u_1(2)u_2(1) \tag{4.42a}$$

Note that if $u_1 = u_2$, the total wave function vanishes. In other words, the probability is zero that the two particles occupy the same quantum state. On the other hand, if symmetrical wave functions such as

$$\psi_s(1,2) = u_1(1)u_2(2) + u_1(2)u_2(1) \tag{4.42b}$$

were allowed, the wave function remains finite when $u_1 = u_2$, and two or more identical particles could then occupy the same quantum state with finite probability. This contradicts all experimental evidence: for example, all the electrons in a multi-electron atom would occupy the same ground state electronic level at low temperature, and the structure of electron configurations leading to the periodic system of elements would be destroyed.

In the more general case when n identical fundamental particles have the independent wave functions $u_1, u_2, \ldots, u_n$ available to them, the antisymmetric wave function for the total system can be expressed as a determinant:

$$\psi_a(1,2,\ldots,n) = \begin{vmatrix} u_1(1) & u_2(1) & \cdots & u_n(1) \\ u_1(2) & u_2(2) & \cdots & u_n(2) \\ \cdot & & & \\ \cdot & & & \\ \cdot & & & \\ u_1(n) & u_2(n) & \cdots & u_n(n) \end{vmatrix} \tag{4.42c}$$

Exchanging any two particles is equivalent to interchanging two rows, which, of course, changes the sign of the determinant. The total wave function may contain factors that are symmetric, but it must contain an odd number of antisymmetric factors to satisfy the Pauli principle.

For the homonuclear diatomic rotator, exchanging the two atoms is equivalent to reversing the radius vector $\vec{r}_0$ (fig. (4.2)), which in polar coordinates is produced by a change in θ of π radians with no change in ϕ. The spherical harmonic functions $Y(\theta,\phi)$ (eq. (4.34)) are even functions of θ when l is even and odd functions of θ when l is odd. To select the appropriate rotational wave function, the symmetry properties associated with nuclear spin must be considered.

4.8 NUCLEAR SPIN

Spin is generally conceded to be a purely quantum phenomenon that has no classical analog (ref. 3). For example, Dirac finds that the relativistic quantum treatment of the electron leads to the two observed spin states of the electron in a natural way, without the need for additional postulates (ref. 4). However, this treatment is so involved that spin is usually explained nonrelativistically as an unknown internal degree of freedom associated with the internal angular momentum of fundamental particles. Such particles must have an angular momentum of $\sqrt{3}\,\hbar/2$ and a degeneracy of 2 to agree with observed facts - such as the measured magnetic moments of protons and electrons, the observed periodic structure of the table of elements, and the fine structure of optical spectra. Accordingly, a spin quantum number $s = 1/2$ is assigned to the internal state of these fundamental particles; the angular momentum is then $\sqrt{s(s + 1)}\,\hbar$ and the degeneracy is $2s + 1$, as required. The orthogonality and symmetry properties of the spin wave functions may be deduced from the commutation rules that exist for angular momentum operators in general, without specifying in analytic detail what those functions are (ref. 1).

Actually, spin need not be treated as a mere formalism. Although the quantitative analysis is very involved, the spin concept is readily appreciated as a direct consequence of the uncertainty principle. A moving particle has an uncertainty in position approximately equal to the De-Broglie wavelength along the direction of the observed momentum vector, but the same particle has uncertainty in position and momentum along the other two directions in space as well. If the situation is described in cylindrical coordinates, this means an uncertainty in the r and θ coordinates and their derivatives about the momentum vector. For r as small as possible, the uncertainty is described by a wave function with either ±1/2 quantum units of angular momentum. The classical analog would describe a particle that corkscrews either clockwise or counterclockwise about the observed momentum vector, with a circular component of velocity c, which adds to the observed linear velocity (see, e.g., Huang's discussion in ref. 5 of the zitterbewegung of the Dirac electron). If the particle is charged, a magnetic moment results, of course. A somewhat simpler semiclassical model treats spin as the quantized rotations of particles with very small but finite moments of inertia, as though the particle consisted of "smeared out" distributions of mass. Such a model gives many qualitative similarities to the actual spin states and therefore has some heuristic value, whatever its other shortcomings.

The two spin wave functions for $s = 1/2$ can be symbolically designated as α and β, without specifying exactly what these functions are. However, they must be orthogonal and normalized with respect to integration over some unspecified spin variable τ, representing the spin degree of freedom:

$$\int \alpha^2\, d\tau = \int \beta^2\, d\tau = 1 \tag{4.43a}$$

$$\int \alpha\beta\, d\tau = 0 \tag{4.43b}$$

Two identical particles (1 and 2) can exist in one antisymmetric spin function:

$$S_a = \frac{1}{\sqrt{2}}\,[\alpha(1)\beta(2) - \alpha(2)\beta(1)] \tag{4.44a}$$

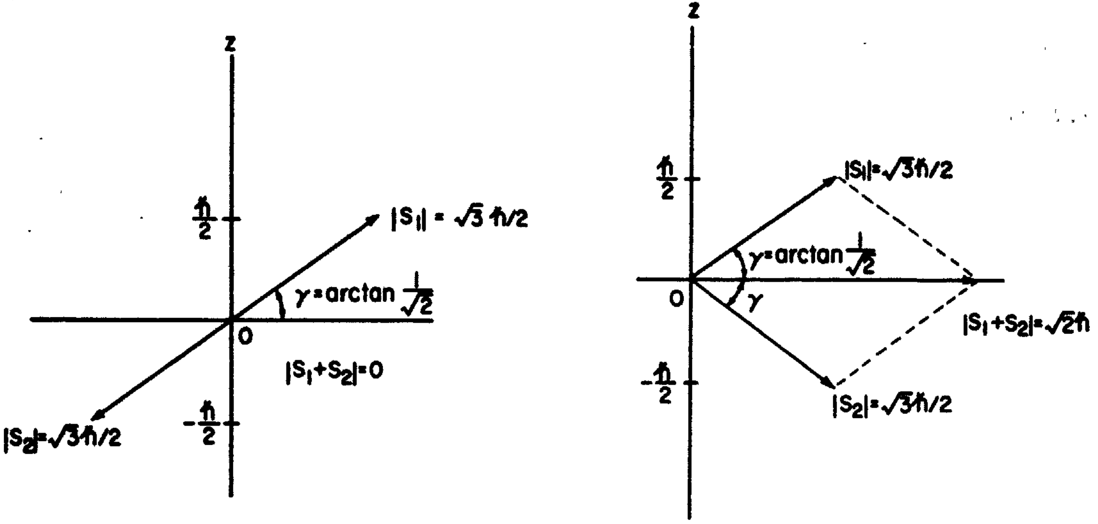
or in any of three symmetric spin functions:

$$S_s = \alpha(1)\alpha(2) \tag{4.44b}$$

$$S_s = \frac{1}{\sqrt{2}}\,[\alpha(1)\beta(2) + \alpha(2)\beta(1)] \tag{4.44c}$$

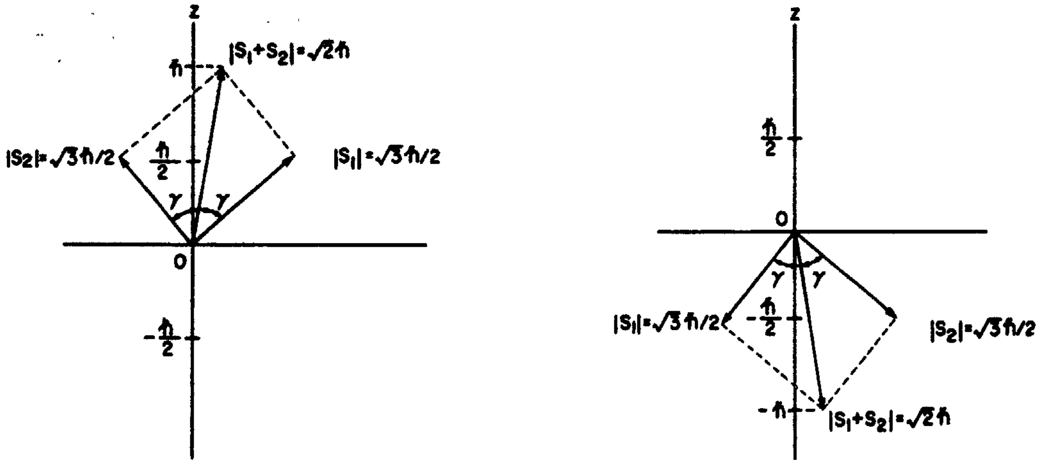
$$S_s = \beta(1)\beta(2) \tag{4.44d}$$

The antisymmetric function (eq. (4.44a)) represent the case when the spins are opposed, the total spin quantum number S and total spin angular momentum are both zero, and the degeneracy $(2S + 1) = 1$. The symmetric spin functions (eqs. (4.44b,c,d)) represent the case when the spins are additive, the total spin quantum number $S = 1$, the total spin angular momentum is $\sqrt{2}\,\hbar$, and the degeneracy $(2S + 1) = 3$. These various spin configurations are diagrammed in figure 4.4.



(a) Antisymmetric spin configuration $S_a = \alpha(1)\beta(2) - \alpha(2)\beta(1)$; total spin $S = 0$.

(b) Symmetric spin configuration $S_s = \alpha(1)\beta(2) + \alpha(2)\beta(1)$; total spin $S = \sqrt{2}\,\hbar$, with zero projection on the polar axis.



(c) Symmetric spin configuration $S_s = \alpha(1)\alpha(2)$; total spin $S = \sqrt{2}\,\hbar$, with projection $\hbar$ on polar axis; S_1 is shown in the plane of the figure, but both S_2 and $S_1 + S_2$ lie out of this plane.

(d) Symmetric spin configuration $S_s = \beta(1)\beta(2)$; total spin $S = \sqrt{2}\,\hbar$, with projection $-\hbar$ on polar axis; S_2 is shown in the plane of the figure and S_1 and $S_1 + S_2$ both lie out of this plane.

Figure 4.4.- Spin momentum and its projections on an axis of symmetry.

Problem 4.5: Verify that the two particle spin functions in equations (4.44) are normalized and are all orthogonal to one another, if the individual spin functions α and β are normalized and orthogonal as defined in equations (4.43).

The notation used for the spin function (4.44c) might, at first glance, suggest that the spins are opposed. However, it means only that the projections of the two spins on a polar axis are opposed (fig. (4.4b)). The paired spin states in equations (4.44c and d) have additive projections on the polar axis and lie in a plane such that each spin projection is $\hbar/2$ and the total spin projection is $\hbar$ on the polar axis (fig. (4.4c)). Note that the expression "parallel spin" means that the spins reinforce one another, not that they are truly parallel in the classical sense.

Problem 4.6: The following problem is designed to convey some heuristic notions about spin with a model that is nonrelativistic, but where the maximum velocity is taken to be the velocity of light and the Einstein equivalence between energy and mass is used. Keep in mind, however, that spin should properly be analyzed by use of the general relativistic relations of accelerated motion.

Consider a hypothetical, nonrelativistic particle with finite moment of inertia. According to fundamental quantum principles of angular momentum operators, such particles can exist (ref. 1) in states with angular momentum $[s(s+1)]^{1/2}\hbar$, which have projections $\pm m\hbar$ on an axis of symmetry, where $m \leq s$ and Δm is an integer (as required by the size of the quantum cell in phase space given by the uncertainty principle). This relation is satisfied if s takes either the integer values 0, 1, 2, 3, . . ., etc., or the half-integer values 1/2, 3/2, 5/2, . . ., etc. The only observed spin state of fundamental particles is $s = 1/2$, and excited spin states are not observed.

When the particle is following a trajectory determined by some potential field, the tangent to the trajectory becomes the axis of symmetry and the wave function in this coordinate has the form e^{ikz} (discussed in ch. 3). However, the particle is also localized in the remaining coordinates, chosen to be the cylindrical coordinates r and ϕ measured relative to the trajectory line. According to the uncertainty principle, the maximum localization (i.e., the smallest average value of r) occurs with the maximum velocity (i.e., the velocity of light). Visualize the particle then with an angular momentum about a point that corresponds to a circular motion with the velocity of light and with a slow drift component along the linear trajectory that corresponds to the linear momentum $k\hbar$.

In terms of a quantum wave function, consider solutions to the Schroedinger equation with $m = 1/2$. Show that, in cylindrical coordinates,

$$\Phi = e^{\pm i\phi/2} \tag{4.45a}$$

satisfies the Schoedinger equation and results in a component of angular momentum along the polar axis

$$p_\phi = -\frac{i\hbar}{\Phi}\frac{d\Phi}{d\phi} = \frac{\hbar}{2}$$

The wave function in equation (4.45a) actually corresponds to a traveling wave with momentum $\hbar/2$ circling the polar axis with wavelength $4\pi r_o$, where r_o is some average radial distance. In steady state, the hypothetical particle with $s = 1/2$ is represented by a standing wave formed from linear combinations of the wave functions given by equation (4.45a)

$$\phi = \frac{1}{\sqrt{\pi}}\cos\frac{\phi}{2}, \qquad \frac{1}{\sqrt{\pi}}\sin\frac{\phi}{2} \tag{4.45b}$$

Show that these spin functions are normalized and orthogonal to one another as required. These functions are not single-valued, of course, but the probability Φ^2 is. Note that the probability is unity that the particle is in one or the other of the two spin states.

The spin wave function might include some function of the radial distance also, but, for present purposes, it is considered to be a delta function $\delta(r_o)$ that represents a thin shell distribution at average distance r_o. To estimate the size of r_o, assume that the rest mass of the hypothetical particle equals the spin energy:

$$mc^2 = s(s+1)\frac{\hbar^2}{2mr_o^2}$$

Find the moment of inertia of such a particle having 1 atomic unit mass (1.66×10^{-24} gm). Find the radius r_o of such a particle if the mass is uniformly distributed in a spherical shell and compare this with the effective radius of protons, known from high-energy scattering measurements to be the order of 10^{-13} cm.

Sometimes it has been suggested that rest mass might be related to the energy of a surface charge of 1 esu placed on a spherical particle. Show that such a charge energy, e^2/r_o, is negligible compared with the spin energy of the above particle.

Show that if an excited state with spin $s = 3/2$ existed without a change in moment of inertia, this would be the order of 10^7 eV above the ground state. For most practical purposes, such a high energy state would not be excited and would remain unobserved. Show that the surface velocity at the equator of the above particles is relativistic in the ground state, so that higher states would correspond to super-relativistic spin velocities and would presumably be unobservable for this reason also. Thus, the maximum possible localization of the spinning sphere, that is, the minimum size r_o, just corresponds to the maximum possible angular momentum and energy for the particle if the velocity of light is assumed to be limiting. Of course, a precise analysis of real spinning particles at these spin velocities would require that mass, size, and angular frequency all be transformed in accord with the general relativity of accelerated motion.

In accord with common usage, spin is hereafter described as having the value s, the spin quantum number, but it should be clearly understood that this means a total spin momentum of $\sqrt{s(s+1)}\,\hbar$.

4.9 ORTHO- AND PARA-SPIN STATES OF HOMONUCLEAR DIATOMIC MOLECULES

Generally, nuclei are a collection of fundamental particles or nucleons (protons and neutrons), all having intrinsic spin $s = 1/2$. The total spin of the nucleus is the algebraic sum of the individual spins

$$s = \sum_i s_i \tag{4.46}$$

A collection of odd-numbered nucleons must have an odd number of half spin units ($s = 1/2, 3/2, 5/2, \ldots$) while an even number of nucleons must have an integral number of spin units ($s = 0, 1, 2, 3, \ldots$). Nuclei with half integer spin are called fermions; they obey Fermi-Dirac statistics because the wave function for a collection of fermions must be antisymmetric with respect to exchange of any two identical fermions, in accord with the Pauli principle. Thus, no two fermions can occupy the same quantum state or cell in phase space. (Examples of fermions are H^1, H^3, He^3, C^{13}, and N^{15}.)

Nuclei composed of an even number of nucleons, and thus with an integer number of spin units, are called bosons; they obey Bose-Einstein statistics because the wave function for a collection of bosons must be symmetric with exchange of any two identical bosons, again in accord with the Pauli principle. (Each boson pair exchanged means exchange of an even number of nucleons, which leaves the wave function unchanged in sign.) Thus, two or more bosons can occupy the same quantum state. (Examples of bosons are H^2, He^4, C^{12}, N^{14}, and O^{16}.)

A diatomic rotator composed of two identical fermions must have the antisymmetric spin function (known as the *para*-state) when the rotational quantum number l is even, but must have a symmetric spin function (known as the *ortho*-state) when l is odd. Then the spin-orbit wave function of the nuclei will be antisymmetric as required by the Pauli principle for exchange of fermions. On the other hand, diatomic rotators composed of two identical bosons must be in the ortho-spin state when l is even, and in the para-spin state when l is odd in order that the spin-orbit wave function be symmetric as required by the Pauli principle for exchange of bosons.

Now consider the H_2 molecule. The H nucleus is a proton with spin 1/2. The para-spin function, corresponding to opposed spins with total spin 0, has a degeneracy of 1; the ortho-spin function, corresponding to parallel spins with a total spin of 1, has a degeneracy of 3. The equilibrium ratio of para- to ortho-H_2 is the ratio of the even and odd rotational state partition functions weighted with the appropriate nuclear spin degeneracy:

$$\frac{H_2(\text{para})}{H_2(\text{ortho})} = \frac{Q_r(\text{even } l)}{3Q_r(\text{odd } l)} = \frac{\sum\limits_{l=0,2,4\ldots} (2l+1)e^{-l(l+1)\theta_r/T}}{3\sum\limits_{l=1,3,5\ldots} (2l+1)e^{-l(l+1)\theta_r/T}} \tag{4.47}$$

At high temperature, the two partition functions both approach $T/2\theta_r$ and the ratio of para- to ortho-H_2 approaches 1/3.

In the more general case, the atoms of a homonuclear diatomic molecule have spin s, which may be any number of half-integer units. The total nuclear spin degeneracy (ref. 2) is

$$g = (2s + 1)^2 \tag{4.48a}$$

corresponding to the fact that the spin of one atom can be oriented $(2s + 1)$ different ways in space, while the spin of the second atom can couple to any one of these in $(2s + 1)$ different ways. The total spin projection on the molecular axis σ thus can take all the integral values from $2s$ to $-2s$. The even functions are those for which σ takes the values (ref. 2)

$$\sigma = 2s,\ 2s - 2,\ 2s - 4,\ \text{etc.} \tag{4.49a}$$

and the odd functions those for which σ becomes

$$\sigma = 2s - 1,\ 2s - 3,\ \text{etc.} \tag{4.49b}$$

There are $s + 1$ different combinations for the even functions, each capable of $(2s + 1)$ different orientations in space. Thus, the degeneracy of ortho-states is

$$g_s = (s + 1)(2s + 1) \tag{4.48b}$$

Similarly, there are s different odd states, again each with $(2s + 1)$ orientations in space, so the degeneracy of para-states is

$$g_a = s(2s + 1) \tag{4.48c}$$

Problem 4.7: Show that if the nuclear spin of the atoms in a homonuclear diatomic molecule is s, the total number of ortho-spin functions given by equation (4.49a) is the sum

$$\sum_{n=0,2,4,\ldots}^{2s-1} [2(2s - n) + 1] = (s + 1)(2s + 1)$$

when $2s$ is odd, and the sum

$$\sum_{n=0,2,4,\ldots}^{2s} [2(2s - n) + 1] = (s + 1)(2s + 1)$$

when $2s$ is even. Also show that the total number of para-spin functions given by equation (4.49b) is the result given by equation (4.48c) in either case.

Next consider the deuterium molecule D_2. The total spin of the D atom can be 0, but this is an excited state. The ground state of the D atom is observed to have spin $s = 1$. Thus, for the D_2 molecule there are six ortho-spin states (eq. (4.48b)) and three para-spin states (eq. (4.48c)). The D atom is a boson, so the total rotational wave function of D_2 must be symmetric. This means that the six ortho-spin states are associated with even orbital momentum states ($l = 0, 2, 4, \ldots$) and three para-spin states are associated with odd orbital momentum states ($l = 1, 3, 5, \ldots$). The equilibrium ratio of ortho- to para-D_2 is thus

$$\frac{D_2(\text{ortho})}{D_2(\text{para})} = \frac{6Q_r(\text{even } l)}{3Q_r(\text{odd } l)} \xrightarrow[T>>\theta_r]{} 2 \tag{4.47a}$$

The normal oxygen atom O^{16} is an interesting boson because its ground state has zero spin. Thus, for the O_2^{16} molecule, the nuclear spin function is ortho with a degeneracy of 1 and the rotational wave function must then be symmetric for the total nuclear wave function to be symmetric. This means that only even-numbered orbital angular momentum states are allowed; this is observed spectroscopically in that every other line in the rotational band structure is missing. On the other hand, the missing lines appear for O^{16}-O^{17} spectra. On a classical basis, one would hardly expect this small difference in nuclear mass to result in such a total effect, and the observed phenomenon constitutes a striking example of the importance of quantum effects. The spectra of other molecules, such as N_2^{14}, also show quantum effects, even where the nuclear spin is not zero; the lines of the rotational band spectra have alternating intensities in proportion to the ratio of para/ortho species. On the other hand, $N^{14}N^{15}$ has equal strength rotational lines.

Collisions can cause conversions between ortho- and para-states, but these occur infrequently because the spins are so weakly coupled to the motion of the nuclei. Transitions are more common in the presence of strong inhomogeneous magnetic fields, or where a paramagnetic collision partner such as O_2 or NO is available to function as a catalyst. Conversions are also produced by dissociation. When the dissociated atoms recombine in the gas, they do so in proportion to the statistical weights of ortho- and para-states. Relatively pure para-H_2 can be prepared in H_2 cooled to near absolute zero temperature. All the para-molecules arrive at the state $l = 0$, and all the ortho-molecules arrive at the state $l = 1$. A catalyst is provided to promote transitions to the lower-lying para-state and is subsequently removed. The pure para-H_2 can then be heated to normal temperatures with essentially no conversion to the ortho-states. Incidentally, ortho-para effects occur wherever rotations can exchange similar atoms, such as in H_2O or CH_4 molecules as well.

4.10 NUCLEAR SPIN ENTROPY

The total partition function of a diatomic rotator should, strictly speaking, include the nuclear spin degeneracy. For the homonuclear diatomic molecule of bosons,

$$Q_r = (s + 1)(2s + 1) \sum_{l=0,2,4,\ldots} (2l + 1)e^{-l(l+1)\theta_r/T}$$

$$+ s(2s + 1) \sum_{l=1,3,5,\ldots} (2l + 1)e^{-l(l+1)\theta_r/T} \tag{4.50a}$$

while a similar expression gives the partition function for a homonuclear diatomic molecule of fermions as

$$Q_r = s(2s + 1) \sum_{l=0,2,4,\ldots} (2l + 1)e^{-l(l+1)\theta_r/T}$$

$$+(s + 1)(2s + 1) \sum_{l=1,3,5,\ldots} (2l + 1)e^{-l(l+1)\theta_r/T} \tag{4.50b}$$

In the limit $T >> \theta_r$, all the summations above approach $T/2\theta_r$ and

$$Q_r \xrightarrow[T>>\theta_r]{} (2s + 1)^2 \frac{T}{2\theta_r} \tag{4.51}$$

which is the same as it was before spin was considered except for the factor $(2s + 1)^2$. A similar factor $(2s + 1)(2s' + 1)$ appears for heteronuclear diatomic molecules (ref. 2), where s and s' are the spins of the two atoms involved. Normally, the symmetry factor 1/2 is retained to differentiate the homonuclear and heteronuclear cases, but the nuclear spin degeneracies are ignored because spin does not change at practical temperatures and the degeneracy is constant (the factor $(2s + 1)(2s' + 1)$ is actually a nuclear spin partition function at the limit where temperature is negligible). This constant factor does not influence any of the thermodynamic properties except to change the reference level of entropy and the free energies. For example (see problem 1.4, ch. 1),

$$S = RT\left(\frac{\partial \ln Q}{\partial T}\right)_p + R \ln \frac{Q}{N} \tag{4.52}$$

In this case, the nuclear spin degeneracy contributes a constant $R \ln[(2s + 1)(2s' + 1)]$ because of the second term on the right in equation (4.52) - referred to as the *nuclear spin entropy*. The entropy disregarding nuclear spin is called the *virtual* or *practical entropy*. For homonuclear diatomic molecules, the subtraction of nuclear spin entropy is applicable only if the ortho/para ratio equals its limiting high-temperature value. Otherwise, the two sums in equation (4.50) do not approach the same value as half the single sum over all states. However, for practical purposes, one can ignore nuclear spin entropy, except for H_2 and D_2 below about 200° K.

Usually, atoms in the ground state have low values of nuclear spin, as spins tend to pair up in the lower energy levels, somewhat similar to electron pairing in atomic and molecular structure. A short list of nuclear spins in ground state atoms is given in table 4.2.

TABLE 4.2.- NUCLEAR SPINS OF GROUND STATE PARTICLES

Particle	e	n	H^1	D^2	H^3	C^{12}	C^{13}	N^{14}	N^{15}	O^{16}	Na	Al	Cl
Spin	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	1	$\frac{1}{2}$	0	$\frac{1}{2}$	1	$\frac{1}{2}$	0	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{5}{2}$

4.11 POLYATOMIC MOLECULE ROTATORS

Any linear molecule is a two-dimensional rotator with two equal and independent moments of inertia about the center of mass and a zero moment about the molecular axis. Then the results are the same as for the diatomic rotator. However, in general, polyatomic molecules have finite moments of inertia in all directions. As for any rigid body, these moments have a vector magnitude that lies along the surface of an ellipsoid. The three perpendicular axes of the ellipsoid, called the principal moments of inertia, are usually indexed in the order of increasing moments ($I_1 \leq I_2 \leq I_3$), sometimes in reverse order. The first convention is followed here.

The derivation of the rotational partition function for an arbitrary three-dimensional body is a somewhat involved but useful exercise, so it is sketched here. Let q_1, q_2, and q_3 be the axes of the principal moments of inertia (I_1, I_2, and I_3). The kinetic energy of the rotator may be expressed as

$$T = \frac{I_1\omega_1^2}{2} + \frac{I_2\omega_2^2}{2} + \frac{I_3\omega_3^2}{2} \tag{4.53}$$

where ω_1, ω_2, and ω_3 are the angular velocities of spin about axes q_1, q_2, and q_3, respectively. The kinetic energy is expressed in terms of the Eulerian angles θ, ϕ, and ψ shown in figure 4.5, which describe the orientation of the rotator with respect to the x, y, z coordinates of space.

Note that $\dot{\psi}$ is the angular velocity about the z axis, $\dot{\phi}$ is the angular velocity about the q_3 axis, and $\dot{\theta}$ is the angular velocity about the nodal line. Take the component of these three independent angular velocity vectors along the q_1, q_2, and q_3 axes and sum like components to find

$$\omega_1 = \dot{\psi}\, sin\, \theta\, sin\, \phi + \dot{\theta}\, cos\, \phi \tag{4.54}$$

$$\omega_2 = \dot{\psi}\, sin\, \theta\, cos\, \phi - \dot{\theta}\, sin\, \phi \tag{4.55}$$

$$\omega_3 = \dot{\psi}\, cos\, \theta + \dot{\phi} \tag{4.56}$$

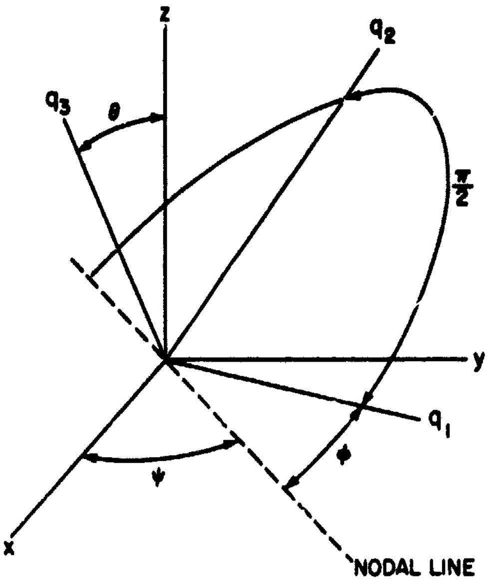


Figure 4.5.- Eulerian angles that define the position of the three principal axes (q_1, q_2, and q_3) for the moment of inertia of the rigid body ellipsoid in x, y, and z space; θ is the angle between q_3 and the z axis. The nodal line is the perpendicular to q_3 which lies in the x-y plane, and ψ is the angle between the nodal line and the x axis. The *arc* symbolizes the plane orthogonal to q_3; that is, the plane defined by the axes q_1 and q_2; φ is the angle between q_1 and the nodal line. Note that some authors use the notation α for ψ, β for θ, and γ for φ, and also sometimes use a left-handed coordinate system in which the x and y axes are interchanged.

Then the total kinetic energy expressed in terms of the Eulerian angles and their derivatives is

$$\begin{aligned} T = {} & \frac{I_1}{2}\left(\dot{\psi}^2 \sin^2\theta \sin^2\phi + 2\dot{\psi}\dot{\theta} \sin\theta \sin\phi \cos\phi + \dot{\theta}^2 \cos^2\phi\right) \\ & + \frac{I_2}{2}\left(\dot{\psi}^2 \sin^2\theta \cos^2\phi - 2\dot{\psi}\dot{\theta} \sin\theta \sin\phi \cos\phi + \dot{\theta}^2 \sin^2\phi\right) \\ & + \frac{I_3}{2}\left(\dot{\psi}^2 \cos^2\theta + 2\dot{\psi}\dot{\phi} \cos\theta + \dot{\phi}^2\right) \end{aligned} \tag{4.57}$$

Since the potential is zero, the kinetic energy expressed in these units is the Lagrangian function $L(q_i,\dot{q}_i)$. The generalized momenta p_i conjugate to the coordinates q_i are, by definition,

$$p_i = \frac{\partial L(q_i,\dot{q}_i)}{\partial \dot{q}_i} = \frac{\partial T}{\partial \dot{q}_i} \tag{4.58}$$

Thus the generalized momenta conjugate to the three Eulerian angles are

$$p_\psi = I_1(\dot\psi \sin^2\theta \sin^2\phi + \dot\theta \sin\theta \sin\phi \cos\phi)$$

$$+I_2(\dot\psi \sin^2\theta \cos^2\phi - \dot\theta \sin\theta \sin\phi \cos\phi)$$

$$+I_3(\dot\psi \cos^2\theta + \dot\phi \cos\theta) \qquad (4.59)$$

$$p_\theta = I_1(\dot\psi \sin\theta \sin\phi \cos\phi + \dot\theta \cos^2\phi)$$

$$-I_2(\dot\psi \sin\theta \sin\phi \cos\phi - \dot\theta \sin^2\phi) \qquad (4.60)$$

$$p_\phi = I_3(\dot\psi \cos\theta + \dot\phi) \qquad (4.61)$$

Now the Hamiltonian for a three-dimensional rigid rotator in terms of the Eulerian angles and their conjugate angular momenta can be written as

$$H = \frac{\cos^2\phi}{2I_1}\left[p_\theta + \frac{\sin\phi}{\sin\theta\cos\phi}(p_\psi - p_\phi\cos\theta)\right]^2$$

$$+ \frac{\sin^2\phi}{2I_2}\left[p_\theta - \frac{\cos\phi}{\sin\theta\sin\phi}(p_\psi - p_\phi\cos\theta)\right]^2$$

$$+ \frac{p_\phi{}^2}{2I_3} \qquad (4.62a)$$

which can be rearranged somewhat to give:

$$H = \frac{1}{2}\left(\frac{\sin^2\phi}{I_2} + \frac{\cos^2\phi}{I_1}\right)\left[p_\theta + \left(\frac{1}{I_1} - \frac{1}{I_2}\right)\frac{\sin\phi\cos\phi(p_\psi - p_\phi\cos\theta)}{\sin\theta\left(\frac{\sin^2\phi}{I_2} + \frac{\cos^2\phi}{I_1}\right)}\right]^2$$

$$+ \frac{1}{2I_1I_2\sin^2\theta}\,\frac{(p_\psi - p_\phi\cos\theta)^2}{\left(\frac{\sin^2\phi}{I_2} + \frac{\cos^2\phi}{I_1}\right)} + \frac{p_\phi{}^2}{2I_3} \qquad (4.62b)$$

This arrangement makes the integrations more straightforward in the phase intergral:

$$Q = \frac{1}{h^3}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} e^{-H/kT}\, dp_\theta\, dp_\phi\, dp_\psi\, d\theta\, d\phi\, d\psi \qquad (4.63)$$

Note that

$$\int_{-\infty}^{\infty} e^{a(x+b)^2}\, dx = \int_{-\infty}^{\infty} e^{ax^2} = \left(\frac{\pi}{a}\right)^{1/2}$$

Integration over p_θ yields a factor

$$\left(\frac{\sin^2\phi}{I_2} + \frac{\cos^2\phi}{I_1}\right)^{-1/2}(2\pi kT)^{1/2}$$

Similar integration next over p_ψ yields the factor

$$\left(\frac{\sin^2\phi}{I_2} + \frac{\cos^2\phi}{I_1}\right)^{1/2} \sin\theta(2\pi kTI_1I_2)^{1/2}$$

Finally, integration over p_ϕ yields the factor

$$(2\pi kTI_3)^{1/2}$$

Integration of the remaining integrand, $\sin\theta$, over all angles θ, ϕ, and ψ yields $8\pi^2$. Thus, for three-dimensional rotators, the partition function is

$$Q = \frac{8\pi^2}{\sigma h^3}(2\pi kT)^{3/2}(I_1I_2I_3)^{1/2} = \frac{1}{\sigma}\left(\frac{T}{\theta_r}\right)^{3/2} \tag{4.64}$$

where the symmetry number σ is again introduced to account for the duplication in the observably different volume of phase space that occurs when the orientation vector of molecules with like atoms is integrated over all 4π steradians. The symmetry numbers for some common polyatomic molecules are listed in table 4.3, for example. The most symmetrical molecule in this table is methane with $\sigma = 12$. Even greater symmetry is possible, sulfurhexafloride, SF_6, for example, has a symmetry number $\sigma = 24$. Herzberg (ref. 6) lists a table of symmetry numbers by point groups, which is a system designating the symmetry of structures according to the mathematics of group theory. The point group to which individual molecules belong is then given at various places in Herzberg's text where these molecules are discussed. The symmetry introduced when some of the atoms are identical produces degeneracy and limits the number of rotational energy levels observed; the more unsymmetrical the molecule, the more levels are observed. Although symmetry effects change the absolute level of entropy, they do not affect the contribution of rotational motions to the equilibrium energy or specific heat per mol.

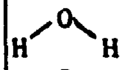
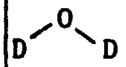
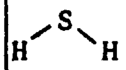
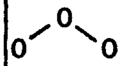
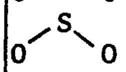
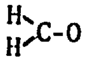
The characteristic rotational temperature defined by equation (4.64) is

$$\theta_r = \frac{\hbar^2}{2k(\pi I_1I_2I_3)^{1/3}} \tag{4.65}$$

A quantity that is normally the order of 10° K or less.

Table 4.3 also gives values of rotational constants, bond angles, and bond lengths (ref. 7) for the polyatomic molecules listed. Just as for Table 4.1, the molecules are assumed to be composed of the most common atomic

TABLE 4.3.- ROTATIONAL CONSTANTS FOR SOME POLYATOMIC MOLECULES

Molecule	Rotational constant, cm^{-1}			Bond angle, deg 2α	Interatomic distance d, Å	Symmetry number σ
	A	B	C			
O-C-O		0.3902		180	1.162	2
S-C-S		.1092		180	1.554 (C-H)	2
H-C-N		1.478		180	1.064 (C-N)	1
N-N-O		0.4190		180	1.126 (N-N) 1.191 (N-O)	1
	27.88	14.51	9.285	105.0	0.9568	2
	15.38	7.25	4.835	105.0	.9568	2
	10.37	8.991	4.732	92.3	1.334	2
	3.553	0.4453	0.3947	116.8	1.278	2
	2.024	.3442	.2935	119.6	1.433	2
H-C-C-H		1.177		180	1.208 (C-C) 1.058 (C-H)	2
	9.410	1.295	1.134	118 (HCH)	1.12 (C-H) 1.21 (C-O)	2
NH_3	9.94	9.94	6.24	106.8 (HNH)	1.014 (N-H)	3
CH_4		5.249		108.0 (HCH)	1.093 (C-H)	12
CH_3Cl	5.097	0.4434	0.4434	110.5 (HCH)	1.781 (C-Cl) 1.113 (C-H)	3

isotopes, and the constants given obtain for the ground vibrational state. Values for other isotope configurations can also be found in reference 7, as well as some values of B_e, α_e, and d_e which obtain at the potential minimums.

4.12 ROTATIONAL ENERGY LEVELS OF NONLINEAR MOLECULES

The classical approximation for the rotational partition function is usually adequate for polyatomic molecules, and this requires only knowledge of the three moments of inertia, I_1, I_2, and I_3. However, these three moments must be deduced from the spacing of rotational energy levels observed by the spectroscopist. In the general case, the three moments are all unequal, the molecule behaves as an asymmetric top, and the rotational energy levels follow a very complex pattern. Deducing the moments is an involved process in this case, and this specialized topic is not pursued here. However, many molecules possess considerable symmetry and can sometimes be treated exactly, or approximately, as symmetric tops, in which case the rotational energy levels follow much simpler patterns. The symmetric top results also serve to give a qualitative concept of the relations that exist between the rotational energy levels and the moments of inertia in the more general case of the asymmetric top.

The classical energy of the rigid rotator given by equation (4.53), but expressed in angular momentum coordinates, is

$$E_r = \frac{P_1{}^2}{2I_1} + \frac{P_2{}^2}{2I_2} + \frac{P_3{}^2}{2I_3} \tag{4.53a}$$

where P_i is the angular momentum about a principal axis i, one of the axes of the moment of inertia ellipsoid. The rotational energy constants A, B, and C are defined as

$$A = \frac{\hbar^2}{2I_1}, \qquad B = \frac{\hbar^2}{2I_2}, \qquad C = \frac{\hbar^2}{2I_3} \tag{4.66}$$

In accord with the convention adopted above ($I_1 \leq I_2 \leq I_3$), the rotational constants are given in the order of decreasing magnitude.

Several limiting cases are of interest. A spherically symmetric top is one where all three moments of inertia are equal ($I_1 = I_2 = I_3$). A prolate symmetric top has one smaller moment of inertia and two larger equal moments ($I_1 < I_2 = I_3$) while an oblate symmetric top has two equal smaller moments and one larger moment ($I_1 = I_2 < I_3$).

Case 1. Spherical Symmetric Top, $I_1 = I_2 = I_3$

The rotational energy can be expressed as

$$E_r = \frac{P_1{}^2 + P_2{}^2 + P_3{}^2}{2I_2} = \frac{P^2}{2I_2} \tag{4.67}$$

where P is the total angular momentum. This quantity is quantized, the wave equation to be solved for the eigenvalues is the same as equation (4.29), so the solutions are

$$P^2 = J(J + 1)\hbar^2 \tag{4.68}$$

$$E_r{}^2 = \frac{\hbar^2}{2I_2} J(J + 1) = BJ(J + 1) \tag{4.69}$$

where J is any integer from 0 to ∞. By convention, J is used for the rotational quantum number for polyatomic molecules (rather than l) and B is used for the rotational constant when a single constant exists. Thus, for spherically symmetric tops, the energy levels follow the same pattern as for the diatomic molecule.

A molecule with equal masses equally spaced in three-dimensional space, such as $C\,Cl_4$, is a spherically symmetric top. Any very large organic molecule of about equal extent in all three dimensions would also be approximately modeled by a spherically symmetric top; only, in this case, internal rotations of parts of the molecule relative to the whole usually occur. Such molecules are not then rigid bodies, and the internal angular momenta couple to the rotation of the whole molecule to present a very complex pattern of rotational energy levels.

Case 2. Prolate Symmetric Top, $I_1 < I_2 = I_3$

Again, let the total angular momentum be quantized as in equation (4.68). The principal axis 1 is now a singular axis of symmetry, and the projection of P on this axis takes quantized values:

$$P_1 = K\hbar \tag{4.70}$$

where K is an integer taking values from $-J$ to J, the exact counterpart of the quantum number m used in equation (4.30). Thus,

$$P_2{}^2 + P_3{}^2 = [J(J+1) - K^2]\hbar^2 \tag{4.71}$$

and the rotational energy in equation (4.53a) becomes

$$E_r = \frac{\hbar^2}{2I_2} J(J+1) + \left(\frac{\hbar^2}{2I_1} - \frac{\hbar^2}{2I_2}\right) K^2$$

$$= BJ(J+1) + (A-B)K^2 \tag{4.72}$$

The $(2J + 1)$ degenerate levels of the spherically symmetric top are now split into $(J + 1)$ different levels, each with a degeneracy of 2 except when $K = 0$. Since $A > B$, the perturbed energy levels all lie above the principal level $BJ(J + 1)$ by amounts proportional to the squares of the integers K.

Methylchloride, CH_3Cl, is an example of a prolate symmetric top ($A = 5.097$ cm^{-1}, $B = C = 0.4434$ cm^{-1}). A molecule such as O_3 has two larger moments of inertia that are nearly equal ($A = 3.55$ cm^{-1}, $B = 0.445$ cm^{-1}, $C = 0.395$ cm^{-1}). In this case, the molecule behaves almost as a prolate symmetric top, and a useful first approximation is to average the two nearly equal rotational constants:

$$\overline{B} = \frac{B + C}{2} \tag{4.73}$$

The energy levels are in this case approximately given by

$$E_r \approx \overline{B}J(J+1) + (A - \overline{B})K^2 \tag{4.74}$$

but the levels with $K \neq 0$ are closely spaced doublets. Mass distributions that are cigar-shaped, rods, discus-shaped, and flat circular plates are examples of prolate symmetric tops. Note that linear molecules ($I_1 = 0$, $I_2 = I_3$)

are a special case of the prolate symmetric top. In this case, the energy levels are independent of K and K is eliminated as a necessary quantum number.

Case 3. Oblate Symmetric Top, $I_1 = I_2 < I_3$

Again, the total angular momentum is quantized as in equation (4.68). Now, however, the principal axis 3 is the singular axis of symmetry, and the projection of P on this axis takes the quantized values:

$$P_3 = K\hbar \tag{4.75}$$

Thus, in this case,

$$P_1^2 + P_2^2 = [J(J + 1) - K^2]\hbar^2 \tag{4.76}$$

and the rotational energy levels are

$$E_r = \frac{\hbar^2}{2I_2} J(J + 1) - \left(\frac{\hbar^2}{2I_2} - \frac{\hbar^2}{2I_3}\right) K^2$$

$$= BJ(J + 1) - (B - C)K^2 \tag{4.77}$$

In this case, the energy levels have a pattern similar to the prolate symmetric top except that it is inverted; all perturbed levels differ from the principal level $BJ(J + 1)$ by amounts proportional to K^2, although in this case lying below the principal level since $B > C$.

Ammonia, NH_3, is an example of an oblate symmetric top ($A = B = 9.94$ cm^{-1}, $C = 6.24$ cm^{-1}). A molecule such as H_2S has two nearly equal smaller moments of inertia ($A = 10.37$ cm^{-1}, $B = 8.991$ cm^{-1}, $C = 4.732$ cm^{-1}) and therefore behaves almost as an oblate symmetric top. Again, a useful first approximation in this case is to average the two nearly equal rotational constants:

$$\overline{B} = \frac{A + B}{2} \tag{4.78}$$

The energy levels are approximately

$$E_r \approx \overline{B}J(J + 1) - (\overline{B} - C)K^2 \tag{4.79}$$

Again, the levels with $K \neq 0$ are closely spaced doublets.

Mass distributions either doughnut-shaped or ring-shaped (such as benzene molecules) are examples of oblate symmetric tops. Derivation of the relations that exist between masses and bond angles in the more general triatomic molecule case is given as the following problem.

Problem 4.8: Show that a nonlinear, symmetric triatomic molecule of the type Y-X-Y (fig. 4.6) has the moments of inertia:

$$I_a = \frac{2m_1 m_2}{2m_1 + m_2} d^2 \cos^2 \alpha \tag{4.80a}$$

$$I_b = 2m_1 d^2 \sin^2 \alpha \tag{4.80b}$$

$$I_c = I_a + I_b \tag{4.80c}$$

where m_1 is the mass of the end atoms, m_2 is the mass of the central atom, d is the bond distance between the central atom and the end atoms, and the angle between these bonds is 2α. Whether I_a or I_b is the smaller thus depends on this angle. The bond length and angle can be determined from the moments of inertia if these can be fit to the observed rotational energy levels

$$d^2 = \frac{I_b}{2m_1} + \frac{I_a}{2m_1}\left(\frac{2m_1 + m_2}{m_2}\right) \tag{4.81}$$

$$\tan^2 \alpha = \left(\frac{m_2}{2m_1 + m_2}\right)\frac{I_b}{I_a} \tag{4.82}$$

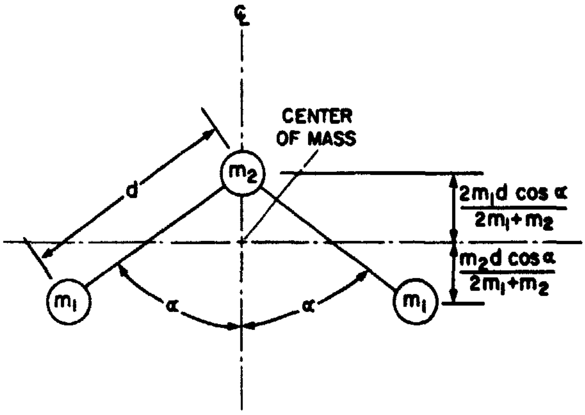


Figure 4.6.- Nonlinear symmetric triatomic molecule; interatomic distance d, included bond angle 2α, mass of end atom m_1, mass of central atom m_2; ——— — ——— axes through center of mass.

Note that a particular angle exists, $\tan \alpha = \sqrt{m_2/(2m_1 + m_2)}$, such that $I_a = I_b = I_c/2$. If the bond angle is close to this angle, as it is for H_2S, the triatomic molecule behaves approximately as an oblate symmetric top. If, on the other hand, the bond angle 2α is near 0 or π, the molecule behaves as a prolate symmetric top. In the former case, $I_a \approx 0$ and $I_b \approx I_c$, while, in the latter case, $I_b \approx 0$ and $I_a = I_c$. At angles rather different than either of these limits or the particular angle $\arctan \sqrt{m_2/(2m_1 + m_2)}$, the molecule behaves as an oblate symmetric top if $m_1 = m_2$ as for O_3, or as an asymmetric top if m_1 and m_2 are rather different as for H_2O. Moments of inertia and bond angles for some typical triatomic molecules are given in table 4.3.

Problem 4.9: Show that the symmetric XY_3 molecule has two equal moments of inertia. Let d be the X-Y bond distance and β be the angle between the X-Y bond and the axis of symmetry. First, let $\beta = 90°$ and show that $I_a = I_b = 2I_c$ for the planar molecule case. Next let the mass of the X atom, m_2, be infinite so that it is located at the center of mass, and show that the moments are $3m_1 d^2 \sin^2 \beta$ and $3m_1 d^2[1 - (1/2)\sin^2 \beta]$, where m_1 is the mass of one Y atom. What is the angle β where the molecule changes from prolate to oblate spherical top? Finally, show that the moments for arbitrary masses are

$$3m_1 d^2 \sin^2 \beta$$

$$\frac{3m_1 d^2}{2(1 + 3m_1/m_2)}\left[2 - \left(1 - \frac{3m_1}{m_2}\right)\sin^2 \beta\right]$$

Calculate the rotational constants for NH_3 where $\beta = 68°$ and $d = 1.014$ Å.

Case 4. Asymmetric Top, $I_1 < I_2 < I_3$

In this case, there are $2J + 1$ distinct energy levels for every value of the rotational quantum number J, and the pattern of levels is more complex than for symmetric tops. If any two moments of inertia are approximately equal, the pattern is similar to that of either a prolate or an oblate symmetric top, with the $K \neq 0$ lines split into closely spaced doublets as mentioned above. If none of the moments are nearly equal, the energy level pattern is distributed above and below an average energy:

$$\overline{E} = \overline{B}J(J + 1) = \frac{1}{3}(A + B + C)J(J + 1) \tag{4.83}$$

In the general case, the pattern can be quite irregular. As an approximation, the energy levels can be taken to be an average of oblate-like top levels and prolate-like top levels

$$E(J,\tau) = \frac{1}{2}\,[E_{obl}(J,i) + E_{pro}(J,j)] \tag{4.84}$$

where τ is an index that runs from $-J$ to J and i and j are indexes such that the lowest levels of E_{obl} and E_{pro} are averaged for the lowest energy ($\tau = -J$), the next to lowest levels are averaged for the next level ($\tau = -J + 1$), and so on. The levels E_{obl} and E_{pro} are given by

$$E_{obl}(J,K) = \left(\frac{A + B}{2}\right) J(J + 1) - \left(\frac{A + B - 2C}{2}\right) K^2 \tag{4.84a}$$

$$E_{pro}(J,K) = \left(\frac{B + C}{2}\right) J(J + 1) + \left(\frac{2A - B - C}{2}\right) K^2 \tag{4.84b}$$

Therefore, the indexes τ, i, and j are related as

$$\begin{array}{lllllll} \tau = -J, & -J+1, & -J+2, & -J+3, & -J+4, & -J+5, & \ldots \\ i = J, & J, & J-1, & J-1, & J-2, & J-2, & \ldots \\ j = 0, & 1, & 1, & 2, & 2, & 3, & \ldots \end{array}$$

If $(A - B) \approx (B - C)$, the pattern is approximately symmetrical; otherwise, the pattern is unsymmetrical. The average energy for a given J is given by equation (4.83) in either case.

The H_2O molecule is an example of a rather asymmetrical top rotator ($A = 27.88\ \text{cm}^{-1}$, $B = 14.51\ \text{cm}^{-1}$, and $C = 9.285\ \text{cm}^{-1}$), with an asymmetrical pattern about the average levels $\overline{B}J(J + 1)$ since $(A - B) \neq (B - C)$. Because the degeneracy of all rotational lines is removed for the asymmetrical top, the H_2O rotation-vibration bands form a closely packed multitude of levels distributed across a major portion of the infrared spectrum. Consequently, the earth's atmosphere is opaque to the peak black-body radiation at the earth's mean temperature, the solar energy received by the earth is effectively trapped and does not reradiate into space and the earth's temperature is maintained at a level habitable for our form of life.

Figure 4.7 shows the types of rotational energy level patterns obtained with the different configurations discussed above: spherically symmetric top, oblate symmetric top, almost oblate symmetric top, asymmetric top, almost prolate symmetric top, and prolate symmetric top. The energy is given in units of $\overline{B}$ as defined in the figure legend for the different cases, so that the principal lines fall at the same point on the energy scale, $J(J + 1)$. Often the energy levels given by equation (4.84a) and (4.84b) are diagrammed on an absolute energy scale; then the levels in equations (4.84) are indicated as a simple average of the corresponding lowest pair of levels, next lowest pair, and so on. Recall that each level of the symmetric tops has a degeneracy of 2 except for $K = 0$, which has a degeneracy of 1. This degeneracy is illustrated in figure 4.8 for levels up to $J = 3$ for $(2/3)A = B = (3/2)C$, which is roughly like the H_2O molecule. The levels predicted by this simple averaging cannot be expected to have high accuracy, of course, but they do give a realistic idea of the spacing and symmetry of the pattern and they are often sufficiently accurate to use in calculating partition functions. If the differences $A - B$ and $B - C$ are more unequal, the pattern becomes more asymmetrical. For higher values of rotational quantum number J, the lines from different J groups overlap and produce a very complex spectrum that is tedious to unravel. An approximation often used in this case is to assume that the $2J + 1$ different levels are randomly distributed in the interval between the minimum level in equation (4.84a) and the maximum level in equation (4.84b).

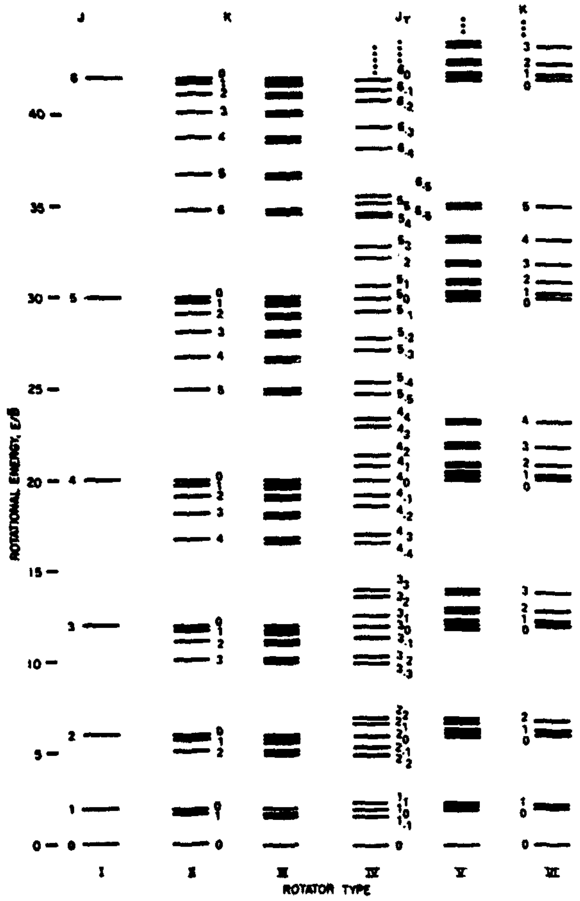


Figure 4.7.- Rotational energy level patterns for polyatomic molecules. Total quantum number, J; projection of J on singular axis of symmetry for symmetric top, K; integer index for lines of asymmetric top, $\tau(-J < \tau < J)$. Type I, spherically symmetric top $(A = B = C)$, also linear molecule $(A = \infty, B = C)$, $\bar{B} = B$; Type II, oblate symmetric top $(A = B > C)$, $\bar{B} = B$, $(B - C = (1/10)B$ for pattern shown); Type III, almost oblate symmetric top $(A \approx B > C)$, $\bar{B} = (1/2)(A + B)$, $(\bar{B} - C = (1/10)\bar{B}$ for pattern shown); Type IV, asymmetric top $(A > B > C)$, $\bar{B} = (1/3)(A + B + C)$, $(A - B \approx B - C \approx (1/10)\bar{B}$ for pattern shown); Type V, almost prolate symmetric top $(A > B \approx C)$, $\bar{B} = (1/2)(B + C)$, $(A - \bar{B} = (1/10)\bar{B}$ for pattern shown); and Type VI, prolate symmetric top $(A > B = C)$, $\bar{B} = B$, $(A - B = (1/10)B$ for pattern shown).

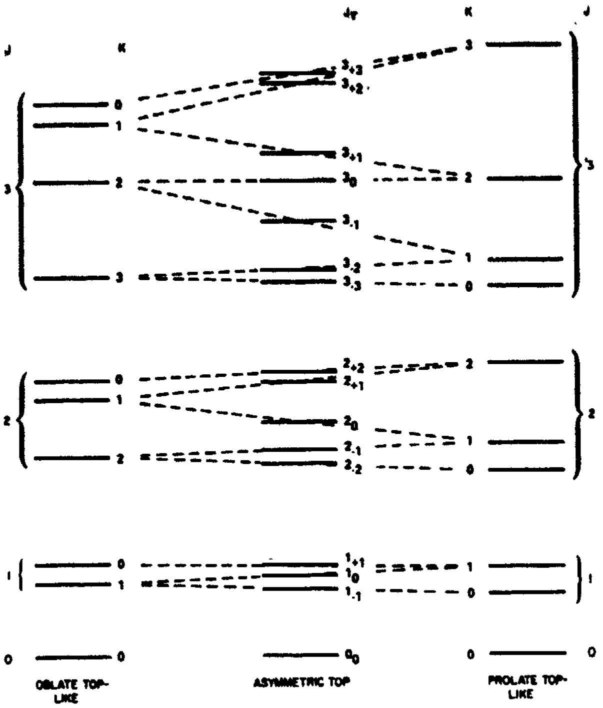


Figure 4.8.- Rotational energy level pattern obtained for asymmetric top by averaging the oblate top and prolate top approximations.

4.13 EQUILIBRIUM ENERGY AND SPECIFIC HEAT OF RIGID ROTATORS

The equilibrium rotational energy of a collection of rigid rotators is given by

$$E_r = RT^2 \frac{d \ln Q_r}{dT} \tag{4.85}$$

The partition function of the two-dimensional rotator is proportional to T, so the equilibrium energy is then

$$E_r \text{ (two-dimensional rotator)} = RT \tag{4.86a}$$

On the other hand, the partition function of the three-dimensional rotator is proportional to $T^{3/2}$, and the equilibrium energy is then

$$E_r \text{ (three-dimensional rotator)} = \frac{3}{2} RT \tag{4.86b}$$

This is an example of equipartition of energy, (1/2)RT being allocated to each of the available degrees of freedom at equilibrium. The specific heats are just the derivatives dE_r/dT:

$$C_v \text{ (two-dimensional)} = R \tag{4.87a}$$

$$C_v \text{ (three-dimensional)} = \frac{3}{2} R \tag{4.87b}$$

Problem 4.10: Develop analytic expressions for the rotational energy, the specific heat, and the entropy for a truncated rigid rotator with maximum quantum number l' given by equation (4.33a).

4.14 CONCLUDING REMARKS

The steady-state wave equation for a two-particle system can, in the absence of external field effects, be decoupled into two independent wave equations, one describing the kinetic energy of the center of mass and the other describing motion of the two particles relative to the center of mass. If the two particles are bound together by a potential, as in a diatomic molecule, the second wave equation describes the rotational and vibrational motions of the molecule.

In many molecules, the amplitudes of vibrational motion are rather small, and to a good approximation the rotational motions may be modeled as a rigid rotating top. Diatomic molecules and linear polyatomic molecules are special cases of prolate symmetric tops and, in this case, the energy levels and rotational contributions to the thermodynamic properties can be analyzed quite rigorously. The polyatomic molecule generally rotates as an asymmetric top; in this case, the energy levels are more difficult to model exactly, but the pattern of levels can be obtained as an average of the prolate-top and oblate-top patterns. The center of these patterns can be accurately placed, so the rotational contributions to thermodynamic properties can be assessed with reasonable accuracy.

Perhaps the most significant contribution gained from the quantum model of rotators is an appreciation of molecular symmetry effects and the role of nuclear spins. These effects do not normally influence the thermodynamic properties of gases appreciably, except for very light molecules at very low temperatures and except for shifting the zero level of entropy. However, nuclear spin effects can strikingly affect the pattern of observed energy levels and the transitions allowed between them.

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CHAPTER 5 - DIATOMIC MOLECULE VIBRATIONS

5.1 SUMMARY

The rotational energy is separated from vibrational energy in the two-particle, steady-state wave equation and to first order the solutions are harmonic oscillator functions. The classical phase integral gives a partition function valid only at high temperature, but the quantum summation is easily performed to give analytic expressions for all the thermodynamic properties of the harmonic oscillator at all temperatures. Anharmonic effects are treated by small perturbation solutions to the wave equation and the relation between energy levels and a series expansion of the perturbation potential is derived. Next, the quantum solutions for an oscillator with a Morse-function potential are derived in terms of Laguerre polynomials.

5.2 INTRODUCTION

The vibrational amplitudes of many molecules are so small that the coupling with rotational motion is relatively modest and to a good approximation the vibrational mode may be treated independently. As gas temperature is increased, a considerable amount of energy can be stored in the vibrational mode, which contributes to the internal energy, specific heat, and other thermodynamic properties of the molecule. Quantum effects are even more pronounced for vibrations than for rotations because the energy spacing between levels is often large compared with normal thermal energies kT. Thus a classical model would be totally inadequate in this case and, for most purposes, a quantum model must be used. In this chapter, we treat the diatomic molecule vibrations and follow with a treatment of polyatomic molecule vibrations in the next chapter.

5.3 DIATOMIC MOLECULE WAVE EQUATIONS

The steady-state, two-particle wave equation in center-of-mass coordinates (derived in ch. 4) is found to be

$$\nabla^2\psi + \frac{2\mu}{\hbar^2}[E - V(r)]\psi = 0 \tag{5.1}$$

For the rigid rotator, the potential $V(r)$ was taken to be zero; now to account for the potential that results from the combination of nuclear coulomb repulsion and the attractive electronic energy:

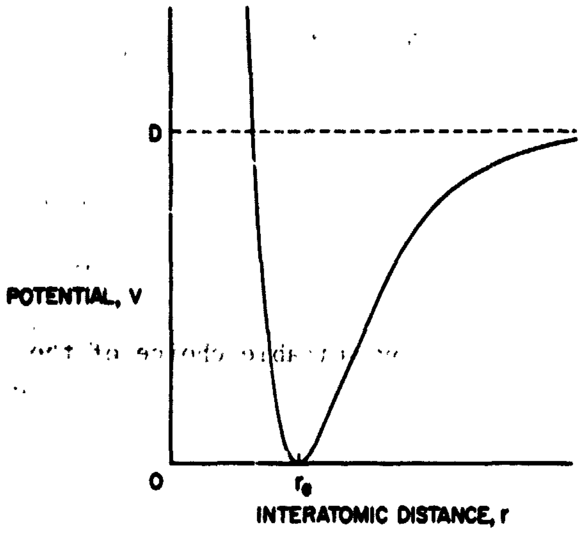

Figure 5.1.- Qualitative shape of interatomic potential in diatomic molecules. The potential is minimum at r_e, it is steeply repulsive at shorter distances, and it asymptotically approaches the dissociation energy D at large r. The shape is approximately quadratic in $(r - r_e)$ near the minimum.

$$V(r) = \frac{e^2 Z_1 Z_2}{r} - E_e(r) \qquad (5.2)$$

where Z_1 and Z_2 are the nuclear charges involved. The electronic interaction E_e is understood qualitatively, and the general shape of the combined attractive potential and the short-range nuclear repulsion is shown in figure 5.1. Unfortunately, accurate quantitative solutions for this potential are not generally available for multielectron atom interactions. However, we can proceed with the empirical observation that most diatomic interaction potentials are very nearly harmonic near the potential minimum, and the lower energy states of vibrational motion at least can be modelled reasonably well with the harmonic oscillator potential

$$V(r) = \frac{\mu\omega^2}{2} (r - r_e)^2 \qquad (5.3)$$

where ω is the circular frequency of the oscillator, $2\pi\nu$, and r_e is the equilibrium interatomic distance. Solutions for harmonic oscillators are considered first and anharmonic effects are treated subsequently.

First the rotational motions are separated from equation (5.1) by assuming a separable wave function in spherical coordinates:

$$\psi(r,\theta,\phi) = \frac{R(r)}{r} Y(\theta,\phi) \qquad (5.4)$$

Substituting equation (5.4) into (5.1) and multiplying by r^2/ψ, one obtains

$$\left\{\frac{r^2}{R}\frac{d^2R}{dr^2} + \frac{2\mu r^2}{\hbar^2}[E - V(r)]\right\} + \frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] = 0 \qquad (5.5)$$

The first bracket in equation (5.5) is a function only of r and the second is a function only of θ and ϕ. Each must be constant, one the negative of the other, for the equation to remain valid for arbitrary r, θ, and ϕ. If the second bracket is equated to $-l(l + 1)$, Y is then the same spherical harmonic function found in chapter 4 to be the solution for the wave function of a rigid rotator with energy $l(l + 1)\hbar^2/2\mu r^2$. The equation for R may be expressed accordingly as

$$\frac{d^2R}{dr^2} + \frac{2\mu}{\hbar^2}\left[E - V(r) - \frac{l(l+1)\hbar^2}{2\mu r^2}\right]R = 0 \tag{5.6}$$

The diatomic oscillator thus behaves in a manner analogous to a single particle of mass μ moving in an effective potential $V(r) + l(l + 1)\hbar^2/2\mu r^2$. Strictly speaking, there is a coupling between the vibrational and rotational energy and the wave function is not truly separable. However, to a first approximation, the vibrational coordinate changes so little from its equilibrium value r_e that the rotational energy term may be replaced with the constant $l(l + 1)\hbar^2/2\mu r_e^2$. To this approximation, the oscillator solutions are independent of rotational quantum number l and, by suitable choice of the reference potential level, the differential equation for the oscillator wave function R has the same form for any value of l:

$$\frac{d^2R}{dr^2} + \frac{2\mu}{\hbar^2}[E_l - V(r)]R = 0 \tag{5.7}$$

where E_l is the energy above the reference level $l(l + 1)\hbar^2/2\mu r_e^2$. Note that this is a one-dimensional, harmonic-oscillator wave equation. The three-dimensional oscillator wave function is YR/r, as given by equation (5.4).

5.4 CLASSICAL HARMONIC OSCILLATOR

The limiting, high-temperature value for the partition function of the harmonic oscillator is the phase integral

$$Q_v \xrightarrow[T\to\infty]{} \frac{1}{h}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-H/kT}\, dp\, dr \tag{5.8}$$

where the Hamiltonian function is the oscillator energy expressed in linear momentum p and distance units r as

$$H = \frac{p^2}{2\mu} + \frac{\mu\omega^2}{2}(r - r_e)^2 \tag{5.9}$$

The integrations in equation (5.8) are easily performed to give

$$Q_v \xrightarrow[T>>\theta_v]{} \frac{kT}{\hbar\omega} = \frac{T}{\theta_v} \tag{5.10}$$

where θ_v is the characteristic temperature

$$\theta_v = \frac{\hbar\omega}{k} \tag{5.11}$$

Unlike the rigid rotator case, where the characteristic temperature was very small, the characteristic vibrational temperature θ_v is rather high for many diatomic gases (see table 5.1). Thus, the summation over quantized states is not accurately reproduced by an integral, as the classical model demands, and the quantum solution is needed for temperatures of practical interest.

TABLE 5.1.- CHARACTERISTIC VIBRATIONAL TEMPERATURES FOR DIATOMIC MOLECULES

(Based on $\omega = \omega_e - \omega_e x_e + 0.75\ \omega_e y_e$, data from ref. 1)

Molecule	$\theta_v = \hbar\omega/k$, °K
O_2	2256
N_2	3371
NO	2719
CO	3103
H_2	6159
D_2	4396
Cl_2	801
Br_2	464
HCl	4228

5.5 QUANTIZED HARMONIC OSCILLATOR

Transform the oscillator coordinate to

$$y = \left(\frac{\mu\omega}{\hbar}\right)^{1/2}(r - r_e) \qquad (5.12)$$

so that the harmonic potential in equation (5.3) becomes $y^2/2$ in units of $\hbar\omega$. Then equation (5.7) becomes

$$\frac{d^2R}{dy^2} + \left[2\left(\frac{E}{\hbar\omega}\right) - y^2\right]R = 0 \qquad (5.13)$$

This equation can be put into the form of Hermite's differential equation by factoring out the asymptotic behavior as $y^2 >> 2E/\hbar\omega$,

$$\frac{d^2R}{dy^2} \xrightarrow[y\to\infty]{} y^2R\ , \qquad R \xrightarrow[y\to\infty]{} e^{-y^2/2}$$

Let $R = e^{-y^2/2}H(y)$. Then equation (5.13) transforms to

$$\frac{d^2H}{dy^2} - 2y\,\frac{dH}{dy} + \left[2\left(\frac{E}{\hbar\omega}\right) - 1\right]H = 0 \qquad (5.14)$$

A series solution with a finite number of terms exists for this equation (refs. 2-3), one of the Hermite polynomials $H_v(y)$, provided the energy is an odd half-integer number of quantum units $\hbar\omega$; that is,

$$\frac{E}{\hbar\omega} = v + \frac{1}{2} \qquad (5.15)$$

where the vibrational quantum number v is any integer from 0 to ∞.

Note that the ground vibrational state contains 1/2 quantum unit of vibrational energy. This occurs because the potential minimum tends to localize the oscillator position and a finite amount of energy must be retained to satisfy the uncertainty principle. For the rigid rotator, no localizing potential was present and the ground rotational state could then be zero energy.

The first few Hermite polynomials are

$$\left.\begin{aligned}
H_0 &= 1 \\
H_1 &= 2y \\
H_2 &= 4y^2 - 2 \\
H_3 &= 8y^3 - 12y \\
H_4 &= 16y^4 - 48y^2 + 12 \\
&\vdots \\
H_v &= \sum_{k=0}^{k_m} \frac{(-1)^k v!}{(v-2k)!\,k!}\,(2y)^{v-2k}
\end{aligned}\right\} \qquad (5.16)$$

where k_m is the largest integer less than or equal to $v/2$. This list may also be extended by means of a recursion relation:

$$H_{v+1} - 2yH_v + 2vH_{v-1} = 0 \qquad (5.17)$$

which is derived in any standard text on quantum mechanics (refs. 2,3).

The one-dimensional, quantized harmonic oscillator wave function now becomes

$$R_v = N_v\, e^{-y^2/2} H_v(y) \qquad (5.18)$$

where N_v is a normalizing constant

$$N_v = \left(\frac{\mu\omega}{\pi\hbar}\right)^{1/4}\left(\frac{1}{2^v v!}\right)^{1/2} \tag{5.19a}$$

so that the integral of R_v^2 over all space is unity:

$$\int_0^\infty R_v^2\,dr = \left(\frac{\hbar}{\mu\omega}\right)^{1/2} N_v^2 \int_{-\sqrt{\mu\omega r_e^2/\hbar}}^{\infty} e^{-y^2} H_v^2\,dy \approx \left(\frac{\hbar}{\mu\omega}\right)^{1/2} N_v^2 \int_{-\infty}^{\infty} e^{-y^2} H_v^2\,dy$$

$$= \left(\frac{\hbar}{\mu\omega}\right)^{1/2} N_v^2 \pi^{1/2} 2^v v! = 1 \tag{5.19b}$$

Evaluation of the integral of $e^{-y^2}H_v^2$ is again available in standard quantum mechanics texts (refs. 2,3). The total three-dimensional, oscillator-rotator wave function, as given by equation (5.4), is

$$\psi_{v,l,m} = \frac{R_v(r)}{r}\,Y_{lm}(\theta,\phi) \tag{5.20}$$

5.6 THERMODYNAMIC FUNCTIONS FOR HARMONIC OSCILLATORS

The degeneracy of each vibrational level for harmonic oscillators is unity and the partition function is a simple geometric progression:

$$Q_v = \sum_{v=0}^{\infty} e^{-v\theta_v/T} = \frac{1}{1 - e^{-\theta_v/T}} \tag{5.21}$$

where the energy levels are defined relative to the ground-state vibrational energy $k\theta_v/2$, the zero point energy referred to in section 1.11. When $T \ll \theta_v$, the partition function approaches unity and the diatomic molecule behaves as a pure rigid rotator. When $T \gg \theta_v$, $Q_v \to T/\theta_v$, the classical limit given by the phase integral, equation (5.10).

The vibrational energy of an equilibrium distribution of harmonic oscillators is

$$E_v - E_o = RT^2\,\frac{d\ln Q_v}{dT} = RT\,\frac{\theta_v/T}{e^{\theta_v/T} - 1} \tag{5.22}$$

where E_o is the molar zero point energy, $R\theta_v/2$. The contribution of the vibrational modes to specific heat and entropy is

$$C_v = \frac{dE_v}{dT} = \frac{R(\theta_v/2T)^2}{sinh^2(\theta_v/2T)} \tag{5.23a}$$

$$S_v = RT\left(\frac{\theta_v/T}{e^{\theta_v/T} - 1}\right) + R\ ln\ Q_v \tag{5.23b}$$

Figure 5.2 shows the variation of E_v/RT and C_v/R as a function of T/θ_v. When $T << \theta_v$, the energy becomes $R\theta_v/2$ or $N\hbar\omega/2$ (the zero point energy for N molecules) and the specific heat vanishes. When $T >> \theta_v$, the energy approaches RT and the specific heat becomes a constant R, the classical limit for two degrees of freedom that depend on quadratic terms in the Hamiltonian (see section 1.10).

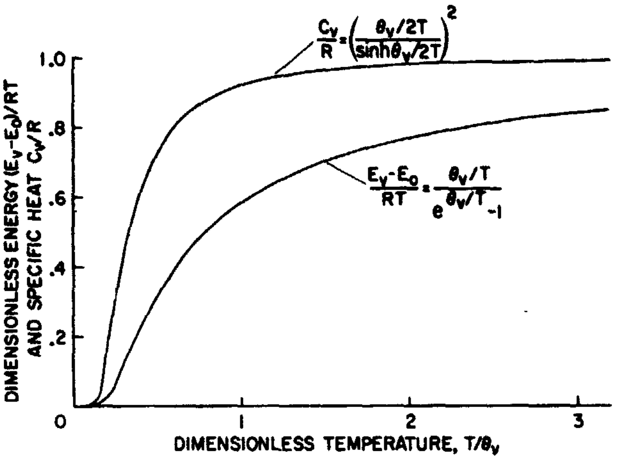

Figure 5.2.- Energy E and specific heat C_v of a harmonic oscillator with characteristic temperature $\theta_v = \hbar\omega/k$. Vibrations are unexcited when $T << \theta_v$ and provide two classical degrees of freedom when $T >> \theta_v$.

The partition function for a real molecule with a finite number of vibrational levels bounded by the dissociation energy D does not increase without limit, as does the harmonic oscillator model with an infinite number of vibrational levels. A qualitative idea of this limit is provided by a truncated harmonic oscillator model with maximum vibrational quantum number $D/k\theta$:

$$Q_v = \sum_{v=0}^{D/k\theta_v} e^{-v\theta_v/T} = \frac{1 - e^{-D/kT}}{1 - e^{-\theta_v/T}} \xrightarrow[T>>D/k]{} \frac{D}{k\theta_v} \tag{5.21a}$$

This limit is the order of 20 or more for many diatomic molecules. At usual temperatures of interest, the correction for truncation of vibrational levels is small and is less important than corrections for anharmonic effects and vibration-rotation coupling. However, it is well to be aware that a finite limit for the vibrational partition function does exist for real molecules, rather than the limitless function deduced from the harmonic oscillator model.

5.7 ANHARMONIC EFFECTS

The intermolecular potential is not purely quadratic, of course, and small deviations from the harmonic oscillator levels occur in real molecules. The observed energy levels are empirically fitted by spectroscopists to a series expansion of the form (refs. 4 and 5)

$$E = \hbar\omega_e\left[\left(v + \frac{1}{2}\right) - x_e\left(v + \frac{1}{2}\right)^2 + y_e\left(v + \frac{1}{2}\right)^3 + \ldots\right] \tag{5.24}$$

where x_e is typically the order of 10^{-2} and y_e, when determined, is generally many orders of magnitude smaller yet. Higher-order terms are usually not warranted despite the magnificent precision of spectroscopic data. The zero level of energy in this expression is the value at the potential minimum, hence the subscript e on ω, x, and y. In older spectroscopic notation, the zero level is the ground-state eigenvalue. The energy function is then expressed as

$$E = \hbar\omega_o[v - x_o v^2 + y_o v^3 + \ldots] \tag{5.24a}$$

and the subscript o denotes the appropriate reference energy.

Problem 5.1: Derive the relations between the spectroscopist's constants ω_o, x_o, y_o and ω_e, x_e, y_e. Show that

$$\omega_o = \omega_e - x_e\omega_e + \frac{3}{4} y_e\omega_e + \ldots$$

$$x_o\omega_o = x_e\omega_e - \frac{3}{2} y_e\omega_e + \ldots$$

$$y_o\omega_o = y_e\omega_e + \ldots$$

One can see that the differences between the two sets of constants are small.

The higher-order terms in the eigenvalues of energy appear when a series expansion is used for the potential function, known as the Dunham potential

$$\frac{V}{\hbar\omega} = \frac{y^2}{2} + ay^3 + by^4 + \ldots \tag{5.25}$$

Fitting higher-order terms than y^4 to the observed energy levels becomes very involved and rarely do the data warrant retention of these higher-order terms. To illustrate the method, retain only the term in y^3; the next order term can be included by following the same procedures, although the process is more involved. In either case, solutions to the Schroedinger equation are obtained by a perturbation method.

5.8 PERTURBATION SOLUTIONS FOR THE STEADY-STATE WAVE EQUATION

The steady-state Schroedinger equation is

$$H\psi = E\psi \tag{5.26}$$

If the Hamiltonian can be expressed as the sum

$$H = H^{o} + H' \tag{5.27}$$

where solutions to the wave equation, ψ_k^{o}, are known for the Hamiltonian H^{o}, the perturbation method can be used. Since solutions to the Schroedinger equation must form an orthogonal set (ref. 2), which can be normalized, the known solutions ψ_k^{o} obey

$$H^{o}\psi_k^{o} = E_k^{o}\psi_k^{o} \tag{5.28}$$

$$\int \psi_k^{o*}\psi_l^{o}\, d\tau = \delta_{kl} = \begin{cases} 1 & \text{if } k = l \\ 0 & \text{if } k \neq l \end{cases} \tag{5.29}$$

The unknown functions ψ_n can be expanded in terms of the orthonormal set of functions ψ_k^{o}:

$$\psi_n = \sum_k a_{nk}\psi_k^{o} \tag{5.30}$$

Substitute equation (5.27) and (5.30) into (5.26) to obtain

$$\sum_k a_{nk}H^{o}\psi_k^{o} + \sum_k a_{nk}H'\psi_k^{o} = \sum_k a_{nk}E_n\psi_k^{o} \tag{5.31}$$

Then, with equation (5.28),

$$\sum_k a_{nk}H'\psi_k^{o} = \sum_k a_{nk}(E_n - E_k^{o})\psi_k^{o} \tag{5.32}$$

Now multiply both sides of equation (5.32) by $(\psi_n^{o})^*$ and integrate over all space. Let the matrix elements U_{ij} denote the integrals

$$U_{ij} = \int \psi_i^{o*}H'\psi_j^{o}\, d\tau \tag{5.33}$$

Then

$$\sum_k a_{nk}U_{nk} = a_{nn}(E_n - E_n^{o}) \tag{5.34}$$

and the perturbed energy is

$$E_n = E_n^o + \sum_k \frac{a_{nk}}{a_{nn}} U_{nk} \tag{5.35}$$

Thus far, no approximation whatever has been involved. Now if H' is small, $\psi_n \approx \psi_n^o$, and to first order the coefficients in equation (5.30) are $a_{nn} \approx 1$, $a_{nk} << 1$. The first-order perturbation result (refs. 2,3) is thus

$$E_n \approx E_n^o + U_{nn} \tag{5.36}$$

For the anharmonic oscillator for which $H' = a\hbar\omega y^3$, the first-order correction vanishes by virtue of symmetry,

$$U_{nn} = a\hbar\omega \int_{-\infty}^{\infty} y^3 (\psi_n^o)^2 \, dy = 0 \tag{5.37}$$

and the next order terms must be considered. Approximate expressions for the coefficients a_{nk} are obtained by multiplying equation (5.32) by $(\psi_l^o)^*$ and integrating over all space:

$$\sum_k a_{nk} U_{lk} = a_{nl}(E_n - E_l^o) \tag{5.38}$$

Again, where $a_{nn} \approx 1$ and all other coefficients are of order much less than unity, the coefficient a_{nl} is given to terms of first order by

$$a_{nl} \approx \frac{U_{ln}}{E_n^o - E_l^o} \tag{5.39}$$

Thus, equation (5.35) can be expanded to

$$E_n = E_n^o + U_{nn} + \sum_{k \neq n} \frac{U_{kn} U_{nk}}{E_n^o - E_k^o} + \ldots \tag{5.40}$$

Equation (5.40) is a general result for any slightly perturbed system. For the case of interest here, a slightly anharmonic oscillator, $E_n^o - E_k^o = (n-k)\hbar\omega$ and $U_{kn} = U_{nk}$. Equation (5.40) thus becomes

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega + U_{nn} + \frac{U_{n,n-1}^2 - U_{n,n+1}^2}{\hbar\omega} + \frac{U_{n,n-2}^2 - U_{n,n+2}^2}{2\hbar\omega} + \frac{U_{n,n-3}^2 - U_{n,n+3}^2}{3\hbar\omega} + \ldots \tag{5.41}$$

The matrix elements U_{nk} are evaluated using the recursion relation between Hermite polynomials given by equation (5.17). Repeated application of the recursion relation leads to

$$y^3H_n = \frac{1}{8}H_{n+3} + \frac{3}{4}(n+1)H_{n+1} + \frac{3n^2}{2}H_{n-1} + n(n-1)(n-2)H_{n-3} \tag{5.42}$$

Since the harmonic oscillator wave functions are orthogonal, the matrix elements U_{nk} all vanish except for $k = n+3$, $n+1$, $n-1$, and $n-3$. The nonvanishing matrix elements,

$$U_{nk} = a\hbar\omega\int_{-\infty}^{\infty} y^3\psi_n{}^o\psi_k{}^o\,dy = a\hbar\omega N_nN_k\int_{-\infty}^{\infty} y^3\,e^{-y^2}H_nH_k\,dy \tag{5.43a}$$

become

$$U_{n,n-1} = \frac{3n^2}{2}\,\frac{N_n}{N_{n-1}}\,a\hbar\omega = \frac{3n^2}{2}\left(\frac{1}{2n}\right)^{1/2}a\hbar\omega \tag{5.43b}$$

$$U_{n,n+1} = \frac{3}{4}(n+1)\,\frac{N_n}{N_{n+1}}\,a\hbar\omega = \frac{3}{4}(n+1)[2(n+1)]^{1/2}a\hbar\omega \tag{5.43c}$$

$$U_{n,n-3} = n(n-1)(n-2)\,\frac{N_n}{N_{n-3}}\,a\hbar\omega = n(n-1)(n-2)\left[\frac{1}{2^3n(n-1)(n-2)}\right]^{1/2}a\hbar\omega \tag{5.43d}$$

$$U_{n,n+3} = \frac{1}{8}\,\frac{N_n}{N_{n+3}}\,a\hbar\omega = \frac{1}{8}[2^3(n+1)(n+2)(n+3)]^{1/2}a\hbar\omega \tag{5.43e}$$

The perturbed energy in equation (5.41) thus becomes

$$\begin{aligned} E_n &= \hbar\omega\left[\left(n+\frac{1}{2}\right) - \frac{9}{8}(3n^2+3n+1)a^2 - \frac{1}{8}(3n^2+3n+2)a^2 + \ldots\right] \\ &= \hbar\omega\left[\left(n+\frac{1}{2}\right) - \frac{15a^2}{4}\left(n+\frac{1}{2}\right)^2 - \frac{7a^2}{16} + \ldots\right] \end{aligned} \tag{5.44}$$

If the small zero point shift in energy level ($7a^2/16$) is neglected, this takes the same form as the spectroscopic notation, equation (5.24), when

$$a^2 = \frac{4x_e}{15} \tag{5.45}$$

Some typical values of x_e are shown in table 5.2, and the difference $7a^2/16$ is truly negligible. We conclude that a cubic anharmonic term in the potential can account for the observed first-order departures from the harmonic oscillator energy levels. However, a quartic perturbation must be included to account for the next order term with coefficient y_e (eq. (5.24)). This next term is derived in a way similar to the derivation just presented.

TABLE 5.2.- ANHARMONIC COEFFICIENTS FOR DIATOMIC MOLECULES

Molecule	x_e	$\hbar\omega/4D$
N_2	0.00612	0.00749
O_2	.00763	.00963
CO	.00620	.00605
NO	.00734	.00909
H_2	.0268	.0304
Cl_2	.00703	.00707
Br_2	.00332	.00508

5.9 MORSE FUNCTION POTENTIAL

The anharmonic effects in the lower vibrational levels can be accounted for adequately by an expansion of the potential function in a power series such as equation (5.25). But near the dissociation limit, such expansions with a practical number of terms will diverge from the true potential. Figure 5.3 shows a harmonic potential adjusted to fit the observed vibrational frequency ω, and an anharmonic cubic potential fit to the observed ω and with a maximum at the dissociation limit. The cubic correction fit to the observed lower energy levels gives a maximum considerably less than D. Both functions diverge from the correct asymptotic value, the dissociation energy, at large values of the interatomic distance. An empirical function that does have the proper asymptotic behavior and that can be closely fit to the observed lower vibrational energy levels is the Morse function (ref. 6):

$$V = D(1 - e^{-x})^2 \qquad (5.46)$$

where the distance variable x is

$$x = \left(\frac{\hbar\omega}{2D}\right)^{1/2} y = \left(\frac{\mu\omega^2}{2D}\right)^{1/2} (r - r_e) \qquad (5.46a)$$

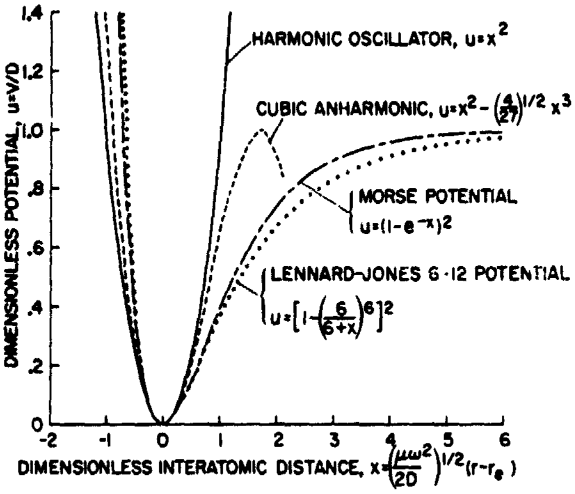

Figure 5.3.- Approximate diatomic molecule potentials. (a) Harmonic oscillator potential that fits the observed vibrational frequency (solid curve). (b) Cubic anharmonic potential that fits the observed ω and has a maximum at the dissociation energy D (dashed curve). (c) Morse potential that fits the observed ω and asymptotically approaches D at large interatomic distances (broken line curve). (d) Lennard-Jones 6-12 potential that fits observed ω and asymptotically approaches D (dotted curve).

This function is also shown in figure 5.3 and, although it closely approaches the asymptotic limit at somewhat larger interatomic distances than observed for most diatomic molecules, the Morse potential gives a more realistic model of upper vibrational levels than the harmonic or power series potentials. An interesting feature of the Morse potential is that exact solutions to the Schroedinger equation can be found (ref. 6). Transform the oscillator wave equation (eq. (5.7)) to the coordinate x in equation (5.46a):

$$\frac{d^2R}{dx^2} + \left(\frac{2D}{\hbar\omega}\right)^2\left(\frac{E}{D} - \frac{V}{D}\right)R = 0 \tag{5.47a}$$

Substitute the Morse potential in equation (5.47a) and let the constant $\alpha = 2D/\hbar\omega$:

$$\frac{d^2R}{dx^2} + \alpha^2\left(\frac{E}{D} - 1 + 2e^{-x} - e^{-2x}\right)R = 0 \tag{5.47b}$$

A further transformation to $w = e^{-x}$ leads to

$$\frac{d^2R}{dw^2} + \frac{1}{w}\frac{dR}{dw} + \alpha^2\left[\frac{(E/D) - 1}{w^2} + \frac{2}{w} - 1\right]R = 0 \tag{5.47c}$$

To transform this into the Laguerre equation, let

$$R(w) = e^{-aw}(2aw)^{b/2}L(w) \tag{5.48}$$

It follows that

$$wL'' + (b + 1 - 2aw)L' + \left[(a^2 - \alpha^2)w + 2\alpha^2 - a(b + 1) + \frac{1}{w}\left(\alpha^2\frac{E}{D} - \alpha^2 + \frac{b^2}{4}\right)\right]L = 0 \tag{5.49}$$

For the expression in brackets, the term in w vanishes if $a = \alpha$ and the term in w^{-1} vanishes if $(E/D) = 1 - b^2/4\alpha^2$. Finally, let $z = 2\alpha w$. Then

$$R(z) = e^{-z/2}z^{b/2}L(z) \tag{5.48a}$$

where $L(z)$ is the solution to the Laguerre equation:

$$z\frac{d^2L}{dz^2} + (b + 1 - z)\frac{dL}{dz} + \left(\alpha - \frac{b + 1}{2}\right)L = 0 \tag{5.49a}$$

This equation has a finite polynomial solution if the coefficient of the last term, $\alpha - (b + 1)/2$, is an integer v. Thus,

$$\frac{b}{2\alpha} = 1 - \frac{v + (1/2)}{\alpha} \tag{5.50}$$

and the allowed energy levels are

$$E_v = D\left[1 - \left(\frac{b}{2\alpha}\right)^2\right] = \frac{2D}{\alpha}\left(v + \frac{1}{2}\right) - \frac{D}{\alpha^2}\left(v + \frac{1}{2}\right)^2$$

$$= \hbar\omega\left[\left(v + \frac{1}{2}\right) - \left(\frac{\hbar\omega}{4D}\right)\left(v + \frac{1}{2}\right)^2\right] \tag{5.51}$$

The factor $\hbar\omega/4D$ is compared with the observed coefficient x_e in table 5.2. Moderate agreement exists between the two; the Morse correction to the harmonic oscillator energy levels is typically 10 to 20 percent too large.

The allowed energy levels are a monatonically increasing function of quantum number v up to $(v + 1/2) \leq 2D/\hbar\omega$. Beyond this, the energy doubles back and finally becomes negative; the levels with decreasing energy as v increases are regarded as unreal and, in this sense, the Morse potential leads to a finite number of levels, approximately the number actually observed.

The solutions to equation (5.49a) are the generalized Laguerre polynomials:

$$L = L^{b}_{v+b}(z) \tag{5.52}$$

The index b need not be integral, but v must be. The complete Morse oscillator wave function is then

$$R_v = C_v \, e^{-z/2} z^{b/2} L^{b}_{v+b}(z) \tag{5.53}$$

where b is given by equation (5.50). The constant C_v is again derived by normalizing the integral of R_v^2 to unity. In terms of the variable z,

$$z = 2\alpha \, e^{-(\mu\omega^2/2D)^{1/2}(r-r_e)} \tag{5.54a}$$

$$dr = -\left(\frac{2D}{\mu\omega^2}\right)^{1/2} \frac{dz}{z} \tag{5.54b}$$

$$1 = \int_0^\infty R_v^2 \; dr = \left(\frac{2D}{\mu\omega^2}\right)^{1/2} \int_0^{2\alpha\, e^{(\mu\omega^2/2D)^{1/2} r_e}} \frac{R_v^2}{z}\, dz \approx \left(\frac{2D}{\mu\omega^2}\right)^{1/2} \int_0^\infty \frac{R_v^2}{z}\, dz \tag{5.55}$$

Thus,

$$C_v^{-2} = \left(\frac{2D}{\mu\omega^2}\right)^{1/2} \int_0^\infty e^{-z} z^{b-1} \left[L^b_{v+b}(z)\right]^2 \, dz \tag{5.56}$$

The integral is evaluated using the moment-generating functions for the Laguerre polynomials:

$$U(u,z) = \sum_{r=b}^{\infty} \frac{L_r^b(z) u^r}{r!} = \frac{(-1)^b \, e^{-zu/(1-u)} u^b}{(1-u)^{b+1}} \tag{5.57a}$$

$$V(y,z) = \sum_{s=b}^{\infty} \frac{L_s^b(z) y^s}{s!} = \frac{(-1)^b \, e^{-zy/(1-y)} y^b}{(1-y)^{b+1}} \tag{5.57b}$$

Consider the integral I defined by

$$I = \int_0^\infty e^{-z} z^{b-1} UV \, dz = \sum_{r,s=b}^{\infty} \frac{u^r y^s}{r!s!} \int_0^\infty e^{-z} z^{b-1} L_r^b L_s^b \, dz$$

$$= \frac{(uy)^b}{(1-u)^{b+1}(1-y)^{b+1}} \int_0^\infty z^{b-1} \; e^{-z[1+(u/1-u)+(y/1-y)]} dz$$

$$= \frac{(uy)^b}{(1-u)^{b+1}(1-y)^{b+1}} \, \frac{(b-1)!}{\left(1 + \dfrac{u}{1-u} + \dfrac{y}{1-y}\right)^b}$$

$$= \frac{(b-1)!}{(1-u)(1-y)} \left(\frac{uy}{1-uy}\right)^b \tag{5.58}$$

Expansion of the factors in the last expression for I yields

$$I = (b-1)! \left(\sum_{j=0}^{\infty} u^j\right)\left(\sum_{k=0}^{\infty} y^k\right)\left[\sum_{l=0}^{\infty} \frac{(b+l-1)!\,(uy)^{b+l}}{(b-1)!\,l!}\right]$$

$$= \sum_{j,k,l=0}^{\infty} \frac{(b+l-1)!}{l!} (uy)^{b+l} u^j y^k \tag{5.59}$$

To evaluate the normalizing integrals, choose those terms where $j = k$, $l + k = n$, and $r = s = n + b$ and compare coefficients:

$$I = \sum_{n=0}^{\infty} (uy)^{n+b} \sum_{l=0}^{n} \frac{(b+l-1)!}{l!} + \text{terms with } \underset{n \neq m}{u^n y^m}$$

$$= \sum_{n=0}^{\infty} \frac{(uy)^{n+b}}{[(n+b)!]^2} \int_0^{\infty} e^{-z} z^{b-1} \left(L_{n+b}^{b}\right)^2 dz + \text{other terms} \tag{5.60}$$

By inspection, one sees that

$$\int_0^{\infty} e^{-z} z^{b-1} \left(L_{n+b}^{b}\right)^2 dz = [(n+b)!]^2 \sum_{l=0}^{n} \frac{(b+l-1)!}{l!} \tag{5.61}$$

and the normalizing constant in equation (5.56) becomes

$$C_v^{-1} = \left(\frac{2D}{\mu\omega}\right)^{1/4} (v+b)! \left[\sum_{l=0}^{v} \frac{(b+l-1)!}{l!}\right]^{1/2} \tag{5.62}$$

Since wave function solutions to Schroedinger's equation must be orthogonal, the overlap integral of Morse functions with different quantum numbers v and v' must vanish. Except for a constant multiplier, these overlap integrals are

$$\int_0^{\infty} e^{-z} z^{-1+(b+c)/2} L_{v+b}^{b} L_{v'+c}^{c}\, dz = \int_0^{\infty} e^{-z} z^{b+\delta-1} L_{v+b}^{b} L_{v+b+\delta}^{b+2\delta}\, dz = 0 \tag{5.63}$$

where δ is the integer $v - v'$, $b = 2\alpha - 2v - 1$, and $c = 2\alpha - 2v' - 1 = b + 2\delta$. This orthogonality may be demonstrated by use of the moment generating function:

$$W(y,z) = \sum_{s=b+2\delta}^{\infty} \frac{L_s^{b+2\delta}}{s!} y^s = \frac{(-1)^{b+2\delta}\, e^{-zy/(1-y)}\, y^{b+2\delta}}{(1-y)^{b+2\delta+1}} \tag{5.57c}$$

along with the moment-generating function $U(u,z)$ in equation (5.57a). Consider the integral

$$I' = \int_0^\infty e^{z} z^{b+\delta-1} UW \, dz = \sum_{\substack{r=b \\ s=b+2\delta}}^{\infty} \frac{u^r y^s}{r!s!} \int_0^\infty e^{-z} z^{b+\delta-1} L_r^b L_s^{b+2\delta} \, dz$$

$$= \frac{u^b y^{b+2\delta}}{(1-u)^{b+1}(1-y)^{b+2\delta+1}} \int_0^\infty z^{b+\delta-1} \; e^{-z[1+(u/1-u)+(y/1-y)]} dz$$

$$= \frac{u^b y^{b+2\delta}}{(1-u)^{b+1}(1-y)^{b+2\delta+1}} \; \frac{(b+\delta-1)!}{\left[\dfrac{1-uy}{(1-u)(1-y)}\right]^{b+\delta}}$$

$$= \frac{(uy)^b}{(1-uy)^{b+\delta}} \, y^{2\delta} \, \frac{(1-u)^{\delta-1}}{(1-y)^{\delta+1}} \, (b+\delta-1)! \qquad (5.64)$$

We are interested in those coefficients where the exponent on y is $r + \delta$, that is, the coefficients of terms with $(uy)^r y^\delta$. But upon expansion of the last expression for I' in equation (5.64) there are no such terms. The expansion of the factor $(1 - u)^{\delta-1}$ is a finite polynomial with $u^{\delta-1}$ as the highest power of u, whereas the expansion of the factor $y^{2\delta}/(1-y)^{\delta+1}$ is an infinite polynomial with $y^{2\delta}$ as the lowest power of y. By inspection then, the integrals described by equation (5.63) all vanish and the Morse wave functions are indeed orthogonal, as required.

5.10 OTHER EMPIRICAL POTENTIAL FUNCTIONS

A number of empirical potential functions other than the Morse function, which also approach the correct asymptotic limit, have been considered. For example, the potential

$$V = \frac{a}{r^{n+m}} - \frac{b}{r^n} + D \qquad (5.65)$$

with a, b, n, and m positive, possesses a short-range repulsion, a long-range attraction, and asymptotically approaches the dissociation energy D at large r. For neutral atom diatomic molecules such as N_2, the attractive potential is primarily associated with induced-dipole, induced-dipole interaction, and n should then be about 6. For ionized diatomic molecules such as N_2^+, the long-range attraction is for a charge-induced dipole pair for which n should be about 4. Ionic binding occurs in highly polar molecules such as HCl, for which the long-range interaction is Coulomb-like and $n \simeq 2$. The widely used Lennard-Jones potential lets $n = m = 6$. The twelfth power repulsion is a fair approximation to the very steep repulsions that actually occur between atoms at short range. In some cases, an exponential repulsion is an even better approximation, so the potential

$$V = a\,e^{-ar} - \frac{b}{r^n} + D \qquad (5.66)$$

is often used. The Lennard-Jones potential fit to the observed vibrational frequency ω at the minimum is also shown in figure 5.3.

Problem 5.2: Show that equation (5.65) with the required shape near the potential minimum $V \xrightarrow[r \to r_e]{} (\mu\omega^2/2)(r - r_e)^2$ can be expressed as

$$\frac{V}{D} = \frac{n}{m}\left(\frac{\beta}{\beta + x}\right)^{n+m} - \frac{n+m}{m}\left(\frac{\beta}{\beta + x}\right)^{n} + 1 \qquad (5.67)$$

where

$$\beta = \left[\frac{n(n+m)}{2}\right]^{1/2}$$

$$x = \left(\frac{\mu\omega^2}{2D}\right)^{1/2}(r - r_e)$$

For $n = m$,

$$\frac{V}{D} = \left[1 - \left(\frac{n}{n+x}\right)^{n}\right]^2$$

and the Lennard-Jones potential is

$$\frac{V}{D} = \left[1 - \left(\frac{6}{6+x}\right)^{6}\right]^2$$

The accuracy of empirical potentials may be assessed by comparing the calculated energy levels with the spectroscopically observed levels; the constant parameters of the potential are then adjusted until the best accuracy is obtained for a given group of levels, usually the low-lying levels near the ground state. This was relatively easy for the Morse function because analytic expressions for the wave functions and the energy levels were obtained. However, analytic solutions have not been found for oscillators with potentials given by equations (5.65) or (5.66). In this case, the Schroedinger equation would need to be solved numerically with the energy level assumed, and this adjustable parameter varied until the solutions to the partial differential equation match the required boundary conditions, namely, that the wave function and all its derivatives must vanish as the oscillator coordinate r becomes very large. These predicted eigenvalues of energy would then be compared with the measured values to assess the accuracy of the empirical potential function.

An easier method of assessing empirical potential functions than presented above is available. The true potential may be deduced from the measured energy levels by a method called the Rydberg-Klein-Rees (RKR) method (refs. 7-9). This need be done only once for a given molecule; then all types of empirical potentials may be compared with the RKR potential. In figure 5.4 for H_2, the Morse potential, the cubic anharmonic potential, and the Lennard-Jones potential, all giving the best fit at the potential minimum, are compared with the accurate Rydberg-Klein-Rees potential for this molecule. The Morse function is the best of these approximations at large values of r.

The Rydberg-Klein-Rees potential may be derived only up to the point where the energy levels are measurable. For some molecules, such as H_2 and O_2, for example, these levels are known nearly to the dissociation limit. The final few levels may be approximated reasonably well by extrapolation (ref. 4). In such cases, the empirical potentials are unnecessary for the accurate evaluation of partition functions, since these may be calculated merely by summing over all measured energy levels. However, for many molecules, the upper vibrational levels are not readily observable for various reasons. Upper levels may not be populated at reasonable temperatures, for example; then the spectroscopist will not see these levels in absorption. In emission spectra, the upper levels may disappear because of predissociation, and transitions to the upper levels of the lower state may be weak because of the small Franck-Condon factors involved (ref. 4). Finally, the energy levels grow very close together near the dissociation limit and line-broadening effects may smear the spectrum together and make it impossible for the spectroscopist to identify the upper states. The N_2 molecule is an example where this uncertainty in the upper states has existed. The extrapolation of measured N_2 vibrational levels was so uncertain that the dissociation energy of N_2 was in doubt for many years (see discussions of this problem by Herzberg (ref. 4) and Gaydon (ref. 5)) until it was finally established with a nonspectroscopic method by Kistiakowsky et al. (ref. 10). In such cases then, the Rydberg-Klein-Rees potential determined to the highest observable vibrational level is the standard used to compare the various empirical potentials having the proper asymptotic limit. The best of these potentials may then be chosen to evaluate the remaining vibrational levels.

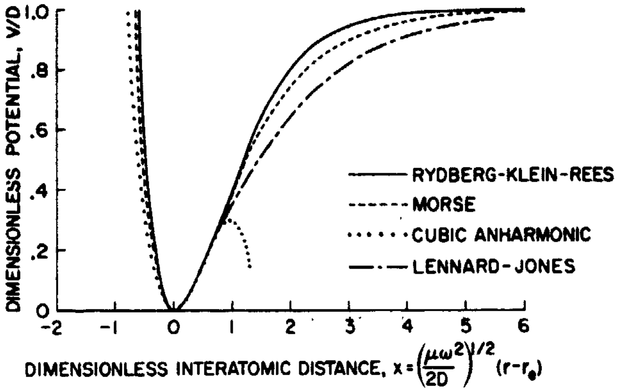

Figure 5.4.- Interatomic potentials for H_2. Rydberg-Klein-Rees potential (solid curve), cubic anharmonic potential (dotted curve), Morse potential (dashed curve), and Lennard-Jones potential (broken line curve).

5.11 RYDBERG-KLEIN-REES POTENTIAL

he Rydberg-Klein-Rees (RKR) potential is the standard by which other potential models are judged (as discussed above), but it also serves another purpose, namely, to provide the most accurate vibrational wave functions whenever these are needed. These wave functions are obtained by successive numerical integration of the Schroedinger equation with the RKR potential function until the eigenvalues are found. Such functions may be needed to determine perturbation transition matrix elements that result from either collision perturbation or photon perturbations. The latter are the so-called

Franck-Condon factors that determine the strength of various rotation-vibration spectral bands (ref. 4), for example. For these reasons, it seems appropriate to review here the method of deriving the RKR potential.

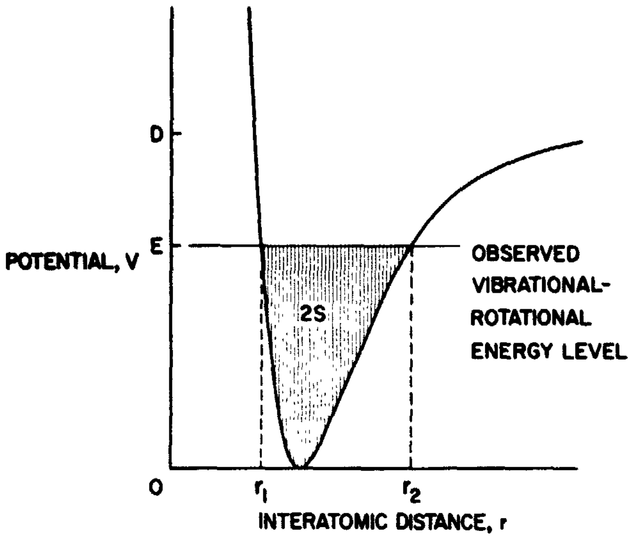

Figure 5.5.- Function $2S$ used to evaluate Rydberg-Klein-Rees potentials (area bounded by total energy E and the interatomic potential V).

Consider the function S that is half the area bounded by the total energy of the oscillator and the interatomic potential (fig. 5.5):

$$2S = \int_{r_1}^{r_2} (E - V)dr \qquad (5.68)$$

The effective potential for rotational quantum level l is, from equation (5.6),

$$V(r) = V_0(r) + \frac{\kappa}{r^2} \qquad (5.69)$$

where $V_0(r)$ is the potential when l is zero and κ is $l(l + 1)\hbar^2/2\mu$. Let functions f and g be defined as

$$f = \left(\frac{\partial S}{\partial E}\right)_\kappa = \frac{1}{2}\int_{r_1}^{r_2} dr = \frac{r_2 - r_1}{2} \qquad (5.70)$$

$$g = -\left(\frac{\partial S}{\partial \kappa}\right)_E = \frac{1}{2}\int_{r_1}^{r_2} \frac{dr}{r^2} = \frac{1}{2}\left(\frac{1}{r_1} - \frac{1}{r_2}\right) \qquad (5.71)$$

Thus, if f and g can be determined for each measured energy level, the turning points of the potential at that energy are given by

$$r_2 = \left(\frac{f}{g} + f^2\right)^{1/2} + f \qquad (5.72)$$

$$r_1 = \left(\frac{f}{g} + f^2\right)^{1/2} - f \qquad (5.73)$$

The area S may be defined in terms of an action integral I that is four times the kinetic energy integrated over time:

$$I = 2\int_{t_1}^{t} \frac{p^2}{\mu}\, dt = 4\int_{t_1}^{t} (E - V)dt \qquad (5.74a)$$

Some authors define the action integral as $I/2\pi$, but this merely changes the constants in the following expressions. The term I must be expressed as a function of r. Since $dr/dt = [2(E - V)/\mu]^{1/2}$,

$$I = (8\mu)^{1/2}\int_{r_1}^{r} (E - V)^{1/2}\, dr \tag{5.74b}$$

$$\frac{dI}{dr} = (8\mu)^{1/2}(E - V)^{1/2} \tag{5.74c}$$

Then the area S may be expressed as

$$2S_v = (8\mu)^{-1/2}\int_0^{I_v} (E_v - V)^{1/2}\, dI \tag{5.75}$$

where the potential V is now considered a function of the action integral I and the quantity κ. The upper limit of the integral in equation (5.75), I_v, is obtained from Planck's first statement of the quantum principle (ref. 2), that is, the area swept out by the trajectory of the system in momentum-coordinate space should equal an integral number of quantum cells of size h:

$$\oint p\, dr = 2\int_{r_1}^{r_2} p\, dr = 2\int_{t_1}^{t_2} \frac{p^2}{\mu}\, dt = I_v = \left(v + \frac{1}{2}\right) h \tag{5.76}$$

The area is increased by $h/2$ to account for the residual motion of the ground state oscillator. This correction is strictly applicable only for the harmonic oscillator, but diatomic molecules are very like harmonic oscillators in the lowest levels, so the correction is sufficiently accurate. Trajectories in momentum-coordinate space are shown in figure 5.6 for a quantized harmonic oscillator and a slightly anharmonic oscillator, indicating how the trajectories gradually diverge while the swept-out areas remain integral multiples of the quantum cell size h.

One can now see how to determine S graphically. Plot $(E_v - E_{v'})^{1/2}$ as a function of $v' + (1/2)$, where the vibrational quantum number v' takes values from 0 to v. Then the area under this curve is multiplied by $h/(32\mu)^{1/2}$ to get S_v. The process is repeated for different values of E_v, but the same rotational quantum number l, to obtain the function S (E_v, constant κ), from which the slope f (eq. (5.70)) is determined. Similarly, repeat the process for the same E_v but different κ or $l(l+1)/2\mu$ to obtain the function S (constant E_v, κ), from which the slope g (eq. (5.71)) is determined. Then the turning points r_1 and r_2 for a given E_v and κ are found from equations (5.72) and (5.73).

For low vibrational levels ($n \leq 5$), there are insufficient points for accurate graphical integration, so a series expansion or Dunham function, equation (5.25), would normally be fit to these lower levels and the RKR

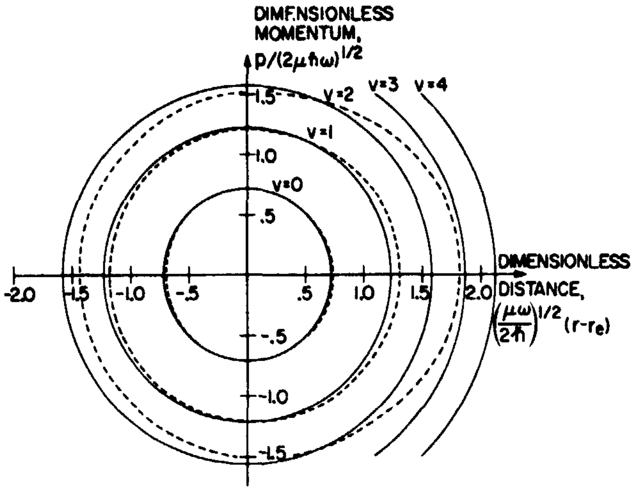

Figure 5.6.- Quantized oscillator trajectories in momentum coordinate space. (a) Harmonic oscillator (solid curves). Momentum intercepts are $p_v = \pm(2\mu E_v)^{1/2} = \pm(2\mu\hbar\omega)^{1/2}\left(v+\frac{1}{2}\right)^{1/2}$, coordinate intercepts are $r_v - r_e = \pm(2E/\mu\omega^2)^{1/2} = \pm(2\hbar/\mu\omega)^{1/2}\left(v+\frac{1}{2}\right)^{1/2}$, trajectories are the ellipses

$$\frac{p^2}{2\mu} + \frac{\mu\omega^2}{2}(r - r_e)^2 = E_v = \left(v+\frac{1}{2}\right)\hbar\omega$$

and the swept-out areas are

$$\oint p\, dr = \pi p_v(r_v - r_e) = \frac{2\pi E_v}{\omega} = \left(v+\frac{1}{2}\right)h$$

(b) Anharmonic oscillator (dashed curves). The intercepts grow increasingly different from the harmonic oscillator intercepts and the trajectories grow increasingly non-elliptic as the quantum number v increases, but the swept-out area increases as integral multiples of the quantum cell size h.

$$\oint p\, dr = vh + \oint p_o\, dr \approx \left(v+\frac{1}{2}\right)h$$

method would then be used to determine the turning points for the higher energy states. However, Vanderslice et al. (ref. 11) use an analytic method to obtain S in which the energy is allowed to be quadratic in I and κ; they find good accuracy is maintained for all levels.

Rydberg's method (ref. 7) is essentially the graphical one outlined above. In Klein's procedure (ref. 8), the integration of equation (5.68) and the differentiations of equations (5.70) and (5.71) are carried out numerically;

the process is laborious and care is necessary to obtain accurate results. Rees (ref. 9) showed that solutions for f and g are readily obtained by analytic means when E_{vl} is expressed as a quadratic relation in I and κ. The usual expression for energy used by spectroscopists is

$$E_{v,l} = hc\left[\omega\left(v+\frac{1}{2}\right) - \omega x\left(v+\frac{1}{2}\right)^2 - \alpha\left(v+\frac{1}{2}\right)l(l+1) + Bl(l+1) + Dl^2(l+1)^2 + \ldots\right] \tag{5.77}$$

where ω, α, B, and D are in cm^{-1}. Define

$$I = \left(v+\frac{1}{2}\right)h \tag{5.78}$$

$$\kappa = \frac{l(l+1)h^2}{8\pi^2\mu} \tag{5.79}$$

Then

$$E = (\omega c)I - \left(\frac{\omega x c}{h}\right)I^2 - \left(\frac{8\pi^2\mu\alpha c}{h^2}\right)I\kappa + \left(\frac{8\pi^2\mu Bc}{h}\right)\kappa + \left(\frac{64\pi^4\mu^2 Dc}{h^3}\right)\kappa^2 + \ldots \tag{5.80}$$

Coupling between rotational levels is included (finite α) since it is required for accurate results. (This coupling effect is discussed in chapter 8.) A single set of values for the constants ω, x, α, B, and D will not fit the energy over the entire range of levels, of course, but the total range can be represented adequately by a series of such quadratics. Vanderslice et al. (ref. 11) use a relatively rapid procedure that fits these constants by least squares to four adjacent observed energy levels. The quadratic relation in equation (5.80) is then used to analytically evaluate the integral S and the differentials f and g. The H_2 molecule is one of the most sensitive tests for accuracy of the method, and good results are obtained for this molecule by the Vanderslice method. Figure 5.4 shows the interatomic potentials for H_2 obtained by Vanderslice et al., the Lennard-Jones function, the Dunham function, and the Morse function. Obviously, the Morse function is the best of the three empirical potential functions at large r.

5.12 THERMODYNAMIC FUNCTIONS FOR ANHARMONIC OSCILLATORS

Simple analytic formulas for the partition function of anharmonic oscillators are normally not derivable, so the function must be evaluated by numerical summation:

$$Q_v = \sum_{v=0}^{v_m} e^{-E_v/kT} \tag{5.81}$$

where E_v is the energy of level v deduced from spectra or given by an approximate expression (such as eq. (5.24) or (5.51)) and v_m is the maximum level allowed by the dissociation limit. The equilibrium vibrational energy and specific heat of a collection of anharmonic oscillators must also be evaluated by numerical summations:

$$\frac{E_v - E_o}{RT} = T\,\frac{d\,ln\,Q_v}{dT} = \frac{1}{Q}\sum_{v=o}^{v_m}\left(\frac{E_v}{kT}\right)e^{-E_v/kT} \tag{5.82}$$

$$\frac{C_v}{R} = \frac{1}{R}\,\frac{dE_v}{dT} = \frac{1}{Q}\sum_{v=o}^{v_m}\left(\frac{E_v}{kT}\right)^2 e^{-E_v/kT} - \left(\frac{E_v - E_o}{RT}\right)^2 \tag{5.83}$$

The entropy due to vibrational modes is just

$$\frac{S_v}{R} = \frac{E_v - E_o}{RT} + ln\,Q_v \tag{5.84}$$

Similarly, all other thermodynamic properties are assessable in terms of the above value of the partition function and its derivatives.

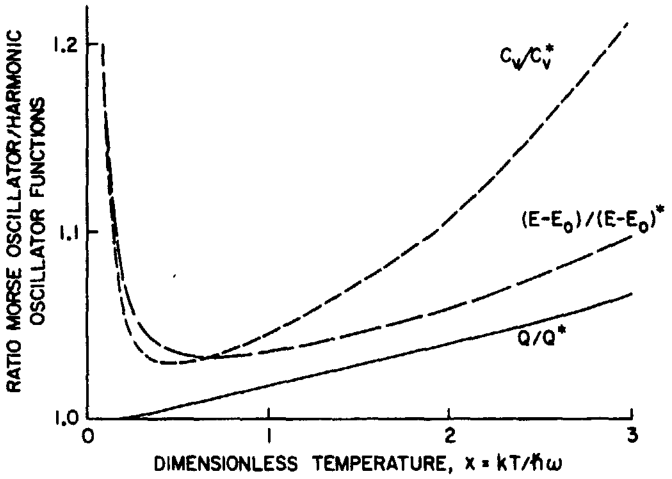

Figure 5.7.- Ratio of Morse oscillator to harmonic oscillator values (superscript *) of the diatomic molecule partition function, energy, and specific heat for $\hbar\omega/4D = 0.009$.

Figure 5.7 shows the ratio of the partition function for a Morse oscillator with $\hbar\omega/4D = 0.009$ (a rather typical value as shown in table 5.2) to the partition function for a harmonic oscillator, plotted as a function of the dimensionless temperature parameter $kT/\hbar\omega$. The ratios of the Morse oscillator vibrational energy and vibrational specific heat to the harmonic oscillator values are also shown. Because the energy levels are more closely spaced in the upper quantum states than for the harmonic oscillator, the partition function, energy, and specific heats are all larger than the harmonic oscillator values. For $kT/\hbar\omega$ up to 3, the corrections range to about 7 percent for the partition function, 10 percent for energy, and 21 percent for specific heat. The correction to the partition function is approximately linear with temperature. An analytic expression for this linear correction is derived in chapter 8 along with some additional linear corrections for vibration-rotation coupling effects. The latter are found to be the same order as the corrections for anharmonic vibrational level spacing so, for economy, these corrections are treated together at that time. The percentage corrections to vibrational energy and specific heat are rather large at low temperatures, but only in the range where their contribution to total energy and specific heat is negligible; the corrections are significant only at temperatures sizable fractions of $\hbar\omega/k$ and larger.

3.13 CONCLUDING REMARKS

Harmonic oscillator solutions adequately represent the vibrational mode of most diatomic molecules in the first few vibrational levels, and small-perturbation corrections account for the anharmonic effects observed in the next few levels. At higher levels, anharmonic effects become sizable. If analytic expressions are desired, the Morse oscillator model gives a very convenient solution that describes the qualitative features of these effects very well with little sacrifice in accuracy. Empirical potential models other than the Morse function can be devised which have the proper asymptotic limit and fit the true potential near the minimum, but these are generally less convenient to use because analytic solutions to Schroedinger's equation are not available. Also, comparisons with the RKR method of evaluating the true potential function show that the Morse function is generally a better approximation than other empirical potential models at large values of the internuclear distance.

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CHAPTER 6 - POLYATOMIC MOLECULE VIBRATIONS

6.1 SUMMARY

Polyatomic molecule vibrations are analyzed as harmonic vibrations along normal coordinates. The energy eigenvalues are found for linear and nonlinear symmetric triatomic molecules for valence bond models of the potential function with arbitrary coupling coefficients; such models can usually be fitted to observed energy levels with reasonably good accuracy. Approximate normal coordinates for the H_2O molecule are discussed. Degenerate vibrational modes such as occur in CO_2 are analyzed and expressions for Fermi resonance between close-lying states of the same symmetry are developed. The bending modes of linear triatomic molecules are expressed in terms of Laguerre polynomials in cylindrical coordinates as well as in terms of Hermite polynomials in Cartesian coordinates. The effects of large-amplitude bending such as occur in the C_3 molecule are analyzed, along with anharmonic effects, which split the usually degenerate bending mode energy levels. Finally, the vibrational frequencies, degeneracies, and symmetry properties of XY_3, X_2Y_2, and XY_4 type molecules are discussed.

6.2 INTRODUCTION

The vibrations of atoms in polyatomic molecules can be approximated by the harmonic oscillator model as well as in diatomic molecules. To decouple the various modes, the energy must be expressed in normal coordinates which, by definition, are those coordinates in which cross-product terms vanish in both the kinetic and potential energy functions.

6.3 NORMAL COORDINATES

Let the position of n nuclei in the molecule be given by Cartesian coordinates of each nucleus relative to its equilibrium position (fig. 6.1):

$$\left.\begin{aligned} q_{3i-2} &= (x - x_e)_i \\ q_{3i-1} &= (y - y_e)_i \\ q_{3i} &= (z - z_e)_i \end{aligned}\right\} \qquad i = 1, 2, \ldots, n \tag{6.1}$$

The kinetic energy can be simply expressed as

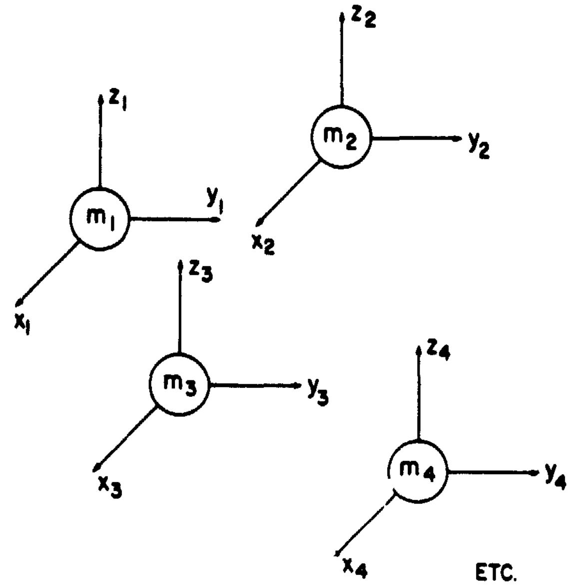

Figure 6.1.- Cartesian coordinates for displacement of atoms from their equilibrium position in polyatomic molecules.

$$T = \frac{1}{2} \sum_{i=1}^{3n} m_i \dot{q}_i^2 \tag{6.2}$$

while the potential energy may be expanded in a Taylor series about the equilibrium position as

$$V = V_e + \sum_i \left(\frac{\partial V}{\partial q_i}\right)_e q_i + \frac{1}{2} \sum_{i,j} b_{ij} q_i q_j + \ldots \tag{6.3}$$

where the coefficients b_{ij} are the second partial derivatives

$$b_{ij} = \left(\frac{\partial^2 V}{\partial q_i \, \partial q_j}\right)_e \tag{6.4}$$

Choose the reference energy so that $V_e = 0$. At equilibrium, the potential is a minimum so the derivatives $(\partial V/\partial q_i)_e$ all vanish. Terms of higher order than second can be neglected for sufficiently small vibrational motion, and thus V may be approximated as

$$V \approx \frac{1}{2} \sum_{i,j} b_{ij} q_i q_j \tag{6.5}$$

The Lagrangian equations of motion then take the form

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{q}_k}\right) + \frac{\partial V}{\partial q_k} = 0 \tag{6.6}$$

$$m_k \ddot{q}_k + \sum_{i=1}^{3n} b_{ik} q_i = 0 , \qquad k = 1, 2, \ldots, 3n \tag{6.7}$$

Generally, these equations are not separable. However, a linear transformation to a new set of coordinates can always be found such that cross-product terms in both equations (6.2) and (6.5) will vanish. These are the normal coordinates Q_k:

$$Q_k = \sum_{i=1}^{3n} \alpha_{ki} q_i , \qquad k = 1, 2, \ldots, 3n \tag{6.8}$$

in which kinetic and potential energies take the form

$$T = \frac{1}{2} \sum_k a_{kk} \dot{Q}_k^2 \tag{6.9}$$

$$V = \frac{1}{2} \sum_k b_{kk} Q_k^2 \tag{6.10}$$

Then the Lagrangian equations of motion becomes

$$a_{kk} \ddot{Q}_k + b_{kk} Q_k = 0 \ , \qquad k = 1, 2, \ldots, 3n \tag{6.11}$$

for which the solutions are

$$Q_k = Q_{k_o} \, e^{i\omega_k t} \tag{6.12a}$$

$$\omega_k = (b_{kk}/a_{kk})^{1/2} \tag{6.12b}$$

where the constants Q_{k_o} are the initial amplitudes. Each normal coordinate Q_k undergoes harmonic motion with frequency ω_k, independently of the motion in the other coordinates. The normal mode concept is a useful approximation to the extent that truncation of the potential energy to include only second-order terms is valid. For large-amplitude vibrations, the higher-order terms become important; then the motion cannot be completely described by a set of normal mode or harmonic motions.

Problem 6.1: Show that if the Hamiltonian is a sum of terms that are each a function of only one coordinate Q_k:

$$H(Q_1, Q_2, \ldots, Q_n) = \sum_{k=1}^{n} H_k(Q_k)$$

the wave function is separable with the form

$$\psi(Q_1, Q_2, \ldots, Q_n) = \prod_{k=1}^{n} \psi_k(Q_k)$$

where the individual mode wave functions ψ_k are solutions to

$$H_k \psi_k = E_k \psi_k$$

and the total energy is the sum

$$E = \sum_{k=1}^{n} E_k$$

Show that where the kinetic and potential energies are the harmonic oscillator expressions in normal coordinates (eqs. (6.9) and (6.10)), the terms in the Hamiltonian are given by

$$H_k = \frac{P_k^2}{2a_{kk}} + \frac{a_{kk}\omega_k^2}{2} Q_k^2$$

where P_k is the generalized momentum conjugate to the coordinate Q_k, the partial derivative of the Lagrangian L (or $T-V$) with respect to $\dot{Q}_k$:

$$P_k = \frac{\partial L}{\partial \dot{Q}_k} = a_{kk}\dot{Q}_k$$

Then the wave equation for ψ_k becomes

$$\frac{d^2\psi_k}{dQ_k^2} - \frac{2a_{kk}}{\hbar^2}\left(E_k - \frac{a_{kk}\omega_k^2}{2} Q_k^2\right)\psi_k = 0$$

Transform to the dimensionless normal coordinate

$$y_k = \left(\frac{a_{kk}\omega_k}{\hbar}\right)^{1/2} Q_k$$

and show that the wave equation for ψ_k becomes

$$\frac{d^2\psi_k}{dy_k^2} - \left(\frac{2E_k}{\hbar\omega_k} - y_k^2\right) = 0$$

for which the solutions are the same harmonic oscillator wave functions

$$\psi_k(v) = N_v\, e^{-y_k^2/2} H_v(y_k)$$

found for the diatomic oscillator.

Generally, finding normal coordinates by diagonalizing the kinetic and potential energy expressions is tedious. However, the equations of motion can be used directly to find the allowed circular frequencies ω_k. Let all amplitude constants Q_{k_o} vanish except one, say Q_{i_o}. Since the q values are related to Q values by the inverse linear transform to equation (6.8);

$$q_k = \sum_{l=1}^{3n} \beta_{kl} Q_l \,, \qquad k = 1, 2, \ldots, 3n \qquad (6.13)$$

each q_k coordinate will also vary harmonically with the same frequency ω when only one normal mode is excited. Let

$$q_k = q_{k_o}\, e^{i\omega t} \,, \qquad k = 1, 2, \ldots, 3n \qquad (6.14)$$

where $q_{k_o} = \beta_{ki} Q_{i_o}$. Substitution of these expressions for q_k into the equations of motion, equation (6.7), yields the set of equations:

$$-\omega^2 m_k q_{k_o} + \left(\sum_{i=1}^{3n} b_{ik} q_{i_o}\right) = 0 \,, \qquad k = 1, 2, \ldots, 3n \qquad (6.15)$$

Equation (6.15) is a set of $3n$ simultaneous equations to be solved for the $3n$ unknowns, q_{k_o}. From the theory of linear algebraic equations, a solution exists only if the following determinant vanishes (refs. 1 and 2):

$$\begin{vmatrix} \left(\dfrac{b_{11}}{m_1} - \omega^2\right) & \dfrac{b_{12}}{m_2} & \cdots & \dfrac{b_{1,3n}}{m_{3n}} \\ \dfrac{b_{21}}{m_1} & \left(\dfrac{b_{22}}{m_2} - \omega^2\right) & \cdots & \dfrac{b_{2,3n}}{m_{3n}} \\ \vdots & \vdots & & \\ \dfrac{b_{3n,1}}{m_1} & \dfrac{b_{3n,2}}{m_2} & \cdots & \left(\dfrac{b_{3n,3n}}{m_{3n}} - \omega^2\right) \end{vmatrix} = 0 \qquad (6.16)$$

This relation provides an equation of degree $3n$ to solve for the allowable values of ω and is known as the secular equation.

In deriving equation (6.15), a coordinate system (fig. 6.1) that diagonalized the kinetic energy expression, equation (6.2), was chosen. However, this is not essential. Sometimes it is most convenient to use symmetry coordinates that do not diagonalize either the potential or kinetic energy expressions. In a general linear transformation of coordinates, the kinetic energy becomes a quadratic expression of the form

$$T = \frac{1}{2} \sum_{ij} a_{ij} \dot{q}_i \dot{q}_j \qquad (6.2a)$$

where the coefficients a_{ij} represent the second partial derivatives of kinetic energy with respect to the generalized velocities $\dot{q}_i$ and $\dot{q}_j$, that is, $(\partial^2 T/\partial \dot{q}_i\, \partial \dot{q}_j)$. In this case, if all normal coordinate amplitude constants are allowed to vanish except one, and equation (6.13) for the coordinate q_k is substituted into the equations of motion,

$$-\omega^2 \left(\sum_{i=1}^{3n} a_{ik} q_{io}\right) + \left(\sum_{i=1}^{3n} b_{ik} q_{io}\right) = 0 , \qquad k = 1, 2, \ldots, 3n \qquad (6.15a)$$

The secular equation to be solved for the allowed roots of ω is, in this general case

$$\begin{vmatrix} (b_{11} - a_{11}\omega^2) & (b_{12} - a_{12}\omega^2) & (b_{13} - a_{13}\omega^2) & \cdots \\ (b_{21} - a_{21}\omega^2) & (b_{22} - a_{22}\omega^2) & (b_{23} - a_{23}\omega^2) & \cdots \\ (b_{31} - a_{31}\omega^2 & (b_{32} - a_{32}\omega^2) & (b_{33} - a_{33}\omega^2) & \cdots \\ \vdots & \vdots & \vdots & \end{vmatrix} = 0 \qquad (6.16a)$$

Often the molecule possesses some symmetry, in which case many of the off-diagonal elements vanish for any plausible model of the potential energy function. Then the secular equation breaks up into a set of lower rank determinants that can be solved more easily. Of course, if the normal coordinates are once found, in which kinetic and potential energy functions have the form of equations (6.9) and (6.10), respectively, then the allowed values of ω are determined most simply from equation (6.12b). As examples, consider linear symmetric triatomic molecules (such as CO_2) and nonlinear symmetric triatomic molecules (such as H_2O).

6.4 LINEAR SYMMETRIC TRIATOMIC MOLECULE XY_2

The linear symmetric triatomic molecule configuration is shown in figure 6.2. Symmetry occurs when the atoms at the end positions are identical. The bond distance between adjacent atoms is d. Consider Cartesian coordinate systems with their origins at the equilibrium position of the atoms and the x axes along the molecular axis. Define the coordinates q_1 and q_2 as the deviation from the equilibrium distances between adjacent atoms:

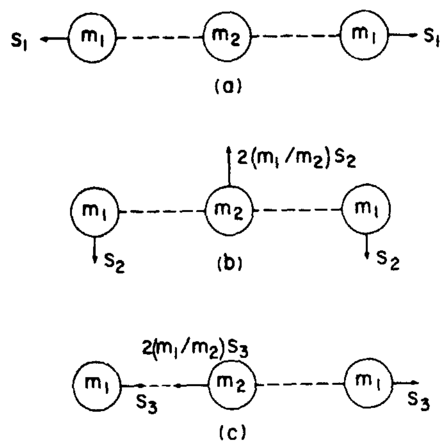

Figure 6.2.- Normal coordinates for linear symmetric triatomic molecules.

$$q_1 = x_2 - x_1 \tag{6.17a}$$

$$q_2 = x_3 - x_2 \tag{6.17b}$$

and the coordinates ϕ_a and ϕ_b as the bending angles in the xy and xz planes, respectively. For very small deflections,

$$\phi_a = \frac{1}{d}\,(y_1 + y_3 - 2y_2) \tag{6.17c}$$

$$\phi_b = \frac{1}{d}\,(z_1 + z_3 - 2z_2) \tag{6.17d}$$

Since the potential energy function is not known, a plausible model must be postulated. The value of the model is then assessed by the accuracy with which it can be fit to spectroscopically observed energy levels. A model that can be reasonably well fit to at least the lower vibrational levels of linear symmetric triatomic molecules is the following:

$$V = \frac{k}{2}\,q_1^2 + \delta q_1 q_2 + \frac{k}{2}\,q_2^2 + \frac{\varepsilon d^2}{2}\,(\phi_a^2 + \phi_b^2) \tag{6.18}$$

The physical interpretation of this model is that k is the force constant for the $X - Y$ bonds, δ is the force constant giving the effect of the interaction between the two bonds, and ε is the force constant for the bending of the molecule. One can anticipate the interaction constant δ to be quite small and, as a first approximation, the simple valence bond model assumes that it vanishes. However, three different harmonic vibrational frequencies are observed experimentally and at least three independent interaction constants are required of any potential model before it can be matched exactly to these observations. (Additional constants would be required to match the observed anharmonic effects, of course, just as for the diatomic molecule.) Therefore, a finite value will be retained for δ to illustrate how the normal mode solutions for triatomic molecule vibrations vary with this parameter. In terms of the Cartesian coordinate system defined in figure 6.1, the potential model in equation (6.18) becomes

$$\begin{aligned} 2V = {} & k(x_1{}^2 - 2x_1x_2 + 2x_2{}^2 - 2x_2x_3 + x_3) \\ & +\delta(2x_1x_2 - 2x_1x_3 - 2x_2{}^2 + 2x_2x_3) \\ & +\varepsilon(y_1{}^2 - 4y_1y_2 + 2y_1y_3 + 4y_2{}^2 - 4y_2y_3 + y_3{}^2 \\ & +z_1{}^2 - 4z_1z_2 + 2z_1z_3 + 4z_2{}^2 - 4z_2z_3 + z_3{}^2) \end{aligned} \qquad (6.19)$$

while the kinetic energy in these coordinates is

$$2T = m_1\dot{x}_1{}^2 + m_2\dot{x}_2{}^2 + m_1\dot{x}_3{}^2 + m_1\dot{y}_1{}^2 + m_2\dot{y}_2{}^2 + m_1\dot{y}_3{}^2 + m_1\dot{z}_1{}^2 + m_2\dot{z}_2{}^2 + m_1\dot{z}_3{}^2 \qquad (6.20)$$

Grouping like terms in the potential equation makes the secular equation (6.16) somewhat easier to set up:

$$\begin{aligned} 2V = {} & kx_1{}^2 - 2(k-\delta)x_1x_2 - 2\delta x_1x_3 \\ & \quad + 2(k-\delta)x_2{}^2 - 2(k-\delta)x_2x_3 + kx_3{}^2 \\ & +\varepsilon y_1{}^2 - 4\varepsilon y_1y_2 + 2\varepsilon y_1y_3 \\ & \quad + 4\varepsilon y_2{}^2 - 4\varepsilon y_2y_3 + \varepsilon y_3{}^2 \\ & +\varepsilon z_1{}^2 - 4\varepsilon z_1z_2 + 2\varepsilon z_1z_3 \\ & \quad + 4\varepsilon z_2{}^2 - 4\varepsilon z_2z_3 + \varepsilon z_3{}^2 \end{aligned} \qquad (6.19a)$$

The secular equation is found to be the product of three 3 × 3 matrices, one of which is

$$\begin{vmatrix} \left(\frac{k}{m_1} - \omega^2\right) & -\left(\frac{k-\delta}{m_2}\right) & -\left(\frac{\delta}{m_1}\right) \\ -\left(\frac{k-\delta}{m_1}\right) & \left(\frac{2k-2\delta}{m_2} - \omega^2\right) & -\left(\frac{k-\delta}{m_1}\right) \\ -\left(\frac{\delta}{m_1}\right) & -\left(\frac{k-\delta}{m_2}\right) & \left(\frac{k}{m_1} - \omega^2\right) \end{vmatrix} = 0 \qquad (6.21a)$$

while the other two are the identical matrices:

$$\begin{vmatrix} \left(\frac{\varepsilon}{m_1} - \omega^2\right) & -\left(\frac{2\varepsilon}{m_2}\right) & \left(\frac{\varepsilon}{m_1}\right) \\ -\left(\frac{2\varepsilon}{m_1}\right) & \left(\frac{4\varepsilon}{m_2} - \omega^2\right) & -\left(\frac{2\varepsilon}{m_1}\right) \\ \left(\frac{\varepsilon}{m_1}\right) & -\left(\frac{2\varepsilon}{m_2}\right) & \left(\frac{\varepsilon}{m_1} - \omega^2\right) \end{vmatrix} = 0 \tag{6.21b}$$

The determinant equation (6.21a) may be solved by subtracting the third column from the first column and then adding the first row to the third row. This operation results in

$$\begin{vmatrix} \left(\frac{k + \delta}{m_1} - \omega^2\right) & -\left(\frac{k - \delta}{m_2}\right) & -\left(\frac{\delta}{m_1}\right) \\ 0 & \left(\frac{2k - 2\delta}{m_2} - \omega^2\right) & -\left(\frac{k - \delta}{m_1}\right) \\ 0 & -\left(\frac{2k - 2\delta}{m_2}\right) & \left(\frac{k - \delta}{m_1} - \omega^2\right) \end{vmatrix} = 0 \tag{6.21c}$$

for which the solution is

$$\left(\frac{k + \delta}{m_1} - \omega^2\right)\left[\omega^4 - \omega^2(k - \delta)\left(\frac{1}{m_1} + \frac{2}{m_2}\right)\right] = 0 \tag{6.21d}$$

The allowed roots for ω^2 are found by setting each factor equal to 0:

$$\omega_1{}^2 = \frac{k + \delta}{m_1} \tag{6.22a}$$

$$\omega_3{}^2 = (k - \delta)\left(\frac{1}{m_1} + \frac{2}{m_2}\right) \tag{6.22b}$$

The third root is found by solving the determinant equation (6.21b). Again, subtracting the third column from the first column and then adding the first row to the third row, one obtains

$$\begin{vmatrix} -(\omega^2) & -\left(\frac{2\varepsilon}{m_2}\right) & \left(\frac{\varepsilon}{m_1}\right) \\ 0 & \left(\frac{4\varepsilon}{m_2} - \omega^2\right) & -\left(\frac{2\varepsilon}{m_1}\right) \\ 0 & -\left(\frac{4\varepsilon}{m_2}\right) & \left(\frac{2\varepsilon}{m_1} - \omega^2\right) \end{vmatrix} = 0 \tag{6.21e}$$

for which the solution is

$$\omega^2\left[\omega^4 - \omega^2 2\varepsilon\left(\frac{1}{m_1} + \frac{2}{m_2}\right)\right] = 0 \tag{6.21f}$$

The nonvanishing root in equation (6.21f) is

$$\omega_2{}^2 = 2\varepsilon\left(\frac{1}{m_1} + \frac{2}{m_2}\right) \tag{6.22c}$$

The allowed values of ω found in equations (6.22a, b, and c) are given the subscripts 1, 2, and 3, according to accepted usage. The circular frequency ω_1 is associated with symmetrical stretching of the molecule, ω_2 is associated with the bending motions, and ω_3, with asymmetrical stretching. Normally, these frequencies are the observables, and the force constants that fit the potential model in equation (6.18) to these frequencies are

$$2k = m_1\omega_1{}^2 + \frac{m_1\omega_3{}^2}{1 + (2m_1/m_2)} \tag{6.23a}$$

$$2\delta = m_1\omega_1{}^2 - \frac{m_1\omega_3{}^2}{1 + (2m_1/m_2)} \tag{6.23b}$$

$$2\varepsilon = \frac{m_1\omega_2{}^2}{1 + (2m_1/m_2)} \tag{6.23c}$$

Problem 6.2: Show that when masses m_1 and m_2 are given in AMU (atomic mass unit, $M = 1.660\times10^{-24}$ gm) and frequencies ω_1, ω_2, and ω_3 in wave numbers, the force constants k, δ, and ε are given in units of $4\pi^2 Mc^2$ or 5.889×10^{-2} dyne-cm. Find the force constants for CO_2 for which $\omega_1 = 1337$ cm^{-1}, $\omega_2 = 667$ cm^{-1}, and $\omega_3 = 2349$ cm^{-1}.

Note that if $\delta = 0$,

$$\omega_1{}^2 = \frac{k}{m_1}\,, \qquad \omega_2{}^2 = \frac{2\varepsilon}{m_1}\left(1 + \frac{2m_1}{m_2}\right), \qquad \omega_3{}^2 = \frac{k}{m_1}\left(1 + \frac{2m_1}{m_2}\right)$$

Find the force constants for CO_2 which fit the potential model with $\delta = 0$. (Two values are obtained for k - one for the observed value of ω_1, another for the observed value of ω_2.) Compare these results with the values found above when δ is given a finite value.

Normal coordinates may generally be rather complex expressions, but for linear triatomic molecules they are rather simple transformations of the Cartesian coordinates shown in figure 6.1, which leave the center of mass unchanged. The linear molecule therefore provides a good example of the use of normal coordinates, without too much algebraic detail.

6.5 NORMAL COORDINATES FOR LINEAR SYMMETRIC TRIATOMIC MOLECULES

A set of normal coordinates S_1, S_2, and S_3, which leaves the center of mass unchanged and causes the cross-product terms to simultaneously vanish in the kinetic energy function and in the potential model in equation (6.18), is shown in figure 6.2 for the linear symmetric triatomic molecule. (S_1 is a symmetric stretching mode, S_3 is an asymmetric stretching mode, and S_2 is a bending mode.) Two independent bending modes, S_{2a} and S_{2b}, occur which are orthogonal to one another; one mode is shown in figure 6.2(b) in the plane of the figure, the second motion occurs in a plane perpendicular to the figure. Multiplication of the coordinates by constants will not change the essential relations involved, provided the center of mass is unchanged. For example, the bending modes could be equally well described by a coordinate change for the end atoms of either m_2S_2 or $m_2S_2/2m_1$ if the center atom motion were taken to be $2m_1S_2$ or S_2, respectively.

The Cartesian coordinates relative to the equilibrium positions shown in figure 6.1 are related to the normal coordinates by

$$\left.\begin{array}{lll} x_1 = -(S_1 + S_3) & y_1 = -S_{2a} & z_1 = -S_{2b} \\ x_2 = \dfrac{2m_1}{m_2} S_3 & y_2 = \dfrac{2m_1}{m_2} S_{2a} & z_2 = \dfrac{2m_1}{m_2} S_{2b} \\ x_3 = S_1 - S_3 & y_3 = -S_{2a} & z_3 = -S_{2b} \end{array}\right\} \tag{6.24}$$

Thus, the kinetic energy in normal coordinates becomes

$$\begin{aligned} T &= \sum_{i=1,2,3} \frac{m_i}{2} (\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2) \\ &= m_1\left[\dot{S}_1^2 + \left(1 + \frac{2m_1}{m_2}\right)(\dot{S}_{2a}^2 + \dot{S}_{2b}^2) + \left(1 + \frac{2m_1}{m_2}\right)\dot{S}_3^2\right] \end{aligned} \tag{6.25}$$

The coordinates in equations (6.17a to d) are

$$q_1 = S_1 + \left(1 + \frac{2m_1}{m_2}\right) S_3 \tag{6.26a}$$

$$q_2 = S_1 - \left(1 + \frac{2m_1}{m_2}\right) S_3 \tag{6.26b}$$

$$\phi_a = -\frac{2}{d}\left(1 + \frac{2m_1}{m_2}\right) S_{2a} \tag{6.26c}$$

$$\phi_b = -\frac{2}{d}\left(1 + \frac{2m_1}{m_2}\right) S_{2a} \tag{6.26d}$$

and the potential energy function in equation (6.18) thus becomes

$$V = (k+\delta)S_1{}^2 + (k-\delta)\left(1+\frac{2m_1}{m_2}\right)^2 S_3{}^2 + 2\varepsilon\left(1+\frac{2m_1}{m_2}\right)^2 (S_{2a}^2 + S_{2b}^2) \qquad (6.27)$$

The normal mode frequencies $\omega_k{}^2$ can be obtained by inspecting equations (6.25) and (6.27) since they are simply the ratio b_{kk}/a_{kk} of the constant coefficients in equations (6.9) and (6.10) (see eq. (6.12b)):

$$\omega_1{}^2 = \frac{b_{11}}{a_{11}} = \frac{k+\delta}{m_1} \qquad (6.28a)$$

$$\omega_2{}^2 = \frac{b_{22}}{a_{22}} = \frac{2\varepsilon}{m_1}\left(1+\frac{2m_1}{m_2}\right) \qquad (6.28b)$$

$$\omega_3{}^2 = \frac{b_{33}}{a_{33}} = \frac{k-\delta}{m_1}\left(1+\frac{2m_1}{m_2}\right) \qquad (6.28c)$$

These results are the same as obtained from solutions to the secular equation (eqs. (6.22a to c)). This example shows that the relations between the force constants and the vibrational frequencies can be found most easily if the normal coordinates are found first. Note, however, that the approximate normal coordinates depend on the potential model chosen.

Problem 6.3: Note that only four of the nine Cartesian coordinates in figure 6.2 are independent; the remaining five are dependent because the center of mass must remain fixed. Choose x_1, x_3, y_1, and z_1 as the set of independent coordinates, then find the remaining Cartesian coordinates in terms of this set. Also show that the normal coordinates are in terms of this set:

$$S_1 = -\frac{1}{2}(x_1 - x_3)$$

$$S_3 = -\frac{1}{2}(x_1 + x_3)$$

$$S_{2a} = -y_1$$

$$S_{2b} = -z_1$$

6.6 NONLINEAR SYMMETRIC TRIATOMIC MOLECULE XY_2

The nonlinear symmetric triatomic molecule is particularly important because the ubiquitous H_2O molecule is a member of this class. In this case, the normal coordinates are not easy to derive, but symmetry coordinates can be found in which the solution to equation (6.16a) becomes relatively easy. More than one set of such symmetry coordinates is possible. For example, the coordinates diagrammed in figures 6.3(a) to (c) are used here, but the coordinates shown in figures 6.3(a') and (b') are alternate choices for the coordinates in figures 6.3(a) and (b), respectively.

The choice of potential function is not an obvious one for the nonlinear molecule. If the angle α is large enough that the end molecules are much farther from one another than from the central atom, a potential of the same form as equation (6.18) should model the molecule reasonably well:

$$V = \frac{k}{2} q_1^2 + \delta q_1 q_2 + \frac{k}{2} q_2^2 + \frac{\varepsilon d^2}{2} \phi^2 \cdot \qquad (6.29)$$

Physically, this represents a harmonic restoring force directed along each valence bond direction with a coupling term and a single harmonic bending mode in the plane of the three atoms. The angle ϕ represents the deviation of α from its equilibrium value. The distance between the end molecules is $2d \sin \alpha$. For H_2O, α is observed to be 52.5°, so the distance between the two H atoms is 1.587 times greater than the distance between the H and O atoms, and equation (6.29) should represent a reasonably good potential model. The angle α is generally 45° or larger in real nonlinear symmetric molecules (see table 4.3); therefore, equation (6.29) is a reasonably good choice in any such case for a potential with three independent force constants that can be fit to the three observed fundamental frequencies.

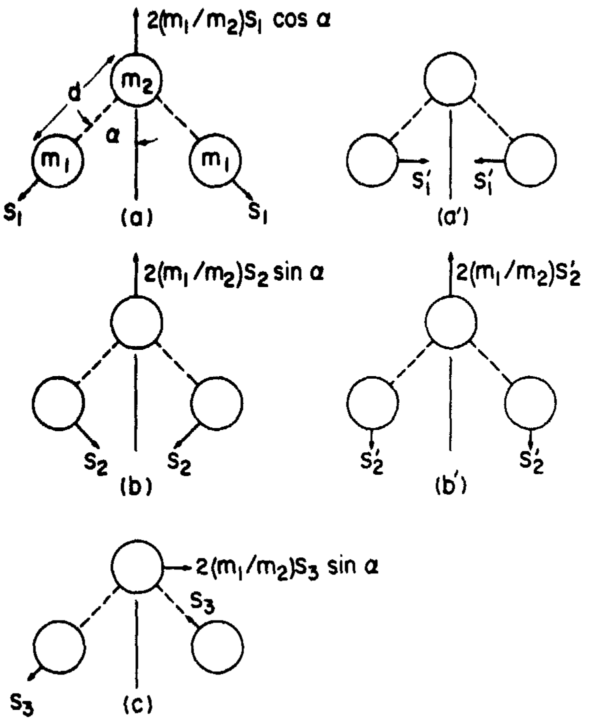

Figure 6.3.- Symmetry coordinates for nonlinear symmetric triatomic molecules.

The coordinates q_1, q_2, and ϕ expressed in the symmetric coordinates in figure 6.3(a) to (c) are

$$q_1 = \left(1 + \frac{2m_1}{m_2} \cos^2 \alpha\right) S_1 + \left(1 + \frac{2m_1}{m_2} \sin^2 \alpha\right) S_3 + \left(\frac{2m_1}{m_2} \sin \alpha \cos \alpha\right) S_2 \qquad (6.30a)$$

$$q_2 = \left(1 + \frac{2m_1}{m_2} \cos^2 \alpha\right) S_1 - \left(1 + \frac{2m_1}{m_2} \sin^2 \alpha\right) S_3 + \left(\frac{2m_1}{m_2} \sin \alpha \cos \alpha\right) S_2 \qquad (6.30b)$$

$$\phi = - \frac{2}{d} \left[\left(\frac{2m_1}{m_2} \sin \alpha \cos \alpha\right) S_1 + \left(1 + \frac{2m_1}{m_2} \sin^2 \alpha\right) S_2\right] \qquad (6.30c)$$

Thus the potential in symmetry coordinates becomes

$$
\begin{aligned}
V = & \left[\left(1 + \frac{2m_1}{m_2} \cos^2 \alpha\right)^2 (k + \delta) + 2\left(\frac{2m_1}{m_2} \sin \alpha \cos \alpha\right)^2 \varepsilon\right] S_1{}^2 \\
& + \left(\frac{4m_1}{m_2} \sin \alpha \cos \alpha\right)\left[\left(1 + \frac{2m_1}{m_2} \cos^2 \alpha\right)(k + \delta) + 2\left(1 + \frac{2m_1}{m_2} \sin^2 \alpha\right)\varepsilon\right] S_1 S_2 \\
& + \left[\left(\frac{2m_1}{m_2} \sin \alpha \cos \alpha\right)^2 (k + \delta) + 2\left(1 + \frac{2m_1}{m_2} \sin^2 \alpha\right)^2 \varepsilon\right] S_2{}^2 \\
& + \left(1 + \frac{2m_1}{m_2} \sin^2 \alpha\right)^2 (k - \delta) S_3{}^2
\end{aligned}
\qquad (6.31)
$$

The kinetic energy in terms of the symmetry coordinates becomes

$$
\begin{aligned}
T = & \frac{m_1}{2} (\dot{S}_1 + \dot{S}_3)^2 + m_1 \dot{S}_2{}^2 + \frac{m_1}{2} (\dot{S}_1 - \dot{S}_3)^2 \\
& + \frac{m_2}{2} \left(\frac{2m_1}{m_2} \dot{S}_1 \cos \alpha + \frac{2m_1}{m_2} \dot{S}_2 \sin \alpha\right)^2 + \frac{m_2}{2} \left(\frac{2m_1}{m_2} \dot{S}_3 \sin \alpha\right)^2
\end{aligned}
\qquad (6.32)
$$

$$
\begin{aligned}
T = m_1 & \left[\left(1 + \frac{2m_1}{m_2} \cos^2 \alpha\right)\dot{S}_1{}^2 + \left(\frac{4m_1}{m_2} \sin \alpha \cos \alpha\right)\dot{S}_1 \dot{S}_2\right. \\
& \left. + \left(1 + \frac{2m_1}{m_2} \sin^2 \alpha\right)\dot{S}_2{}^2 + \left(1 + \frac{2m_1}{m_2} \sin^2 \alpha\right)\dot{S}_3{}^2\right]
\end{aligned}
\qquad (6.33)
$$

The partial derivatives a_{ij} and b_{ij} defined by equations (6.2a) and (6.4), respectively, are easily deduced by inspection of equations (6.31) and (6.33) to be

$$
\left.
\begin{aligned}
b_{11} &= \left(1 + \frac{2m_1}{m_2} \cos^2 \alpha\right)^2 (k + \delta) + 2\left(\frac{2m_1}{m_2} \sin \alpha \cos \alpha\right)^2 \varepsilon \\
b_{12} = b_{21} &= \left(\frac{2m_1}{m_2} \sin \alpha \cos \alpha\right)\left[\left(1 + \frac{2m_1}{m_2} \cos^2 \alpha\right)(k + \delta) + 2\left(1 + \frac{2m_1}{m_2} \sin^2 \alpha\right)\varepsilon\right] \\
b_{22} &= \left(\frac{2m_1}{m_2} \sin \alpha \cos \alpha\right)^2 (k + \delta) + 2\left(1 + \frac{2m_1}{m_2} \sin^2 \alpha\right)^2 \varepsilon \\
b_{33} &= \left(1 + \frac{2m_1}{m_2} \sin^2 \alpha\right)^2 (k - \delta) \\
a_{11} &= m_1\left(1 + \frac{2m_1}{m_2} \cos^2 \alpha\right) \\
a_{12} = a_{21} &= m_1\left(\frac{2m_1}{m_2} \sin \alpha \cos \alpha\right) \\
a_{22} = a_{33} &= m_1\left(1 + \frac{2m_1}{m_2} \sin^2 \alpha\right)
\end{aligned}
\right\}
\qquad (6.34)
$$

The remaining second derivatives b_{23} and a_{23} vanish because of the choice of symmetry coordinates. Thus, the secular equation (6.16a), for the allowed circular frequencies, becomes

$$\begin{vmatrix} (b_{11} - a_{11}\omega^2) & (b_{12} - a_{12}\omega^2) & 0 \\ (b_{12} - a_{12}\omega^2) & (b_{22} - a_{22}\omega^2) & 0 \\ 0 & 0 & (b_{33} - a_{33}\omega^2) \end{vmatrix} = 0 \qquad (6.35)$$

One root of the equation is immediately apparent

$$\omega_3{}^2 = \frac{b_{33}}{a_{33}} = \left(1 + \frac{2m_1}{m_2}\, sin^2\ \alpha\right) \frac{k - \delta}{m_1} \qquad (6.36)$$

Note that this reduces to the same value given by equation (6.22b) for the linear symmetric triatomic molecule when $\alpha = \pi/2$. The other two roots are solutions to the quadratic equation

$$(a_{11}a_{22} - a_{12}^2)\omega^4 - (a_{11}b_{22} - 2a_{12}b_{12} + a_{22}b_{11})\omega^2 + (b_{11}b_{22} - b_{12}^2) = 0 \qquad (6.37)$$

In the present case, the coefficients of this quadratic equation are

$$a = a_{11}a_{22} - a_{12}^2 = m_1{}^2\left(1 + \frac{2m_1}{m_2}\right) \qquad (6.38a)$$

$$b = a_{11}b_{22} - 2a_{12}b_{12} + a_{22}b_{11} = m_1\left(1 + \frac{2m_1}{m_2}\, cos^2\ \alpha\right)\left(1 + \frac{2m_1}{m_2}\right)(k + \delta)$$

$$+2m_1\left(1 + \frac{2m_1}{m_2}\, sin^2\ \alpha\right)\left(1 + \frac{2m_1}{m_2}\right)\varepsilon \qquad (6.38b)$$

$$c = b_{11}b_{22} - b_{12}^2 = 2\left(1 + \frac{2m_1}{m_2}\right)^2 (k + \delta)\varepsilon \qquad (6.38c)$$

The solutions for ω^2 may be characterized rather simply by the sum and product of the roots:

$$\omega_1{}^2 + \omega_2{}^2 = \frac{b}{a} = \left(1 + \frac{2m_1}{m_2}\, cos^2\ \alpha\right)\frac{k + \delta}{m_1} + 2\left(1 + \frac{2m_1}{m_2}\, sin^2\ \alpha\right)\frac{\varepsilon}{m_1} \qquad (6.39)$$

$$\omega_1{}^2\omega_2{}^2 = \frac{c}{a} = 2\left(1 + \frac{2m_1}{m_2}\right)\frac{(k + \delta)\varepsilon}{m_1{}^2} \qquad (6.40)$$

Again, these are the same expressions obtained for the linear symmetric molecule when $\alpha = \pi/2$.

Problem 6.4: The observed fundamental frequencies and bond angles for H_2O are $\omega_1 = 3652\ cm^{-1}$, $\omega_2 = 1595\ cm^{-1}$, $\omega_3 = 3756\ cm^{-1}$, and $2\alpha = 105°$. Solve for the values of k, δ, and ε that fit the potential model in equation (6.29) to these values. Show that

$$k = 7.62\times10^5 \text{ dyne-cm}$$

$$\delta = -9.43\times10^3 \text{ dyne-cm}$$

$$\epsilon = 6.97\times10^4 \text{ dyne-cm}$$

Note that the coupling coefficient δ is negative rather than positive, as for CO_2.

Problem 6.5: Another potential model often used is the harmonic, three-valance-bond model without cross-coupling. The deviation from equilibrium distance between the end atoms is

$$q_3 = 2d\phi \cos\alpha$$

and the potential in equation (6.29) with $\delta = 0$ becomes

$$V = \frac{k}{2}q_1{}^2 + \frac{k}{2}q_2{}^2 + \frac{k'}{2}q_3{}^2$$

where

$$k' = \frac{\epsilon}{4\cos^2\alpha}$$

This potential model might be expected to be reasonably valid if α is the order of $\pi/3$ so that the three atoms are approximately equally spaced. Another constant would be required to fit the three observed frequencies, of course, but the model would give approximately valid results if the cross-couplings are all small.

Show that

$$\omega_3{}^2 = \left(1 + \frac{2m_1}{m_2}\sin^2\alpha\right)\frac{k}{m_1}$$

$$\omega_1{}^2 + \omega_2{}^2 = \left(1 + \frac{2m_1}{m_2}\cos^2\alpha\right)\frac{k}{m_1} + \frac{8k'}{m_1}\cos^2\alpha\left(1 + \frac{2m_1}{m_2}\sin^2\alpha\right)$$

$$\omega_1{}^2\omega_2{}^2 = 8\left(1 + \frac{2m_1}{m_2}\right)\cos^2\alpha\,\frac{kk'}{m_1{}^2}$$

Note that the solution breaks down for $\alpha = \pi/2$ since the last equation requires that ω_1 or ω_2 vanish. However, for the usual nonlinear, symmetric triatomic molecule, α is the order of $\pi/4$, and the results are similar to the results in equations (6.36), (6.39), and (6.40).

6.7 APPROXIMATE NORMAL COORDINATES FOR H_2O

The normal coordinates for nonlinear molecules are not generally aligned with the interatomic distance vectors and they are rather involved expressions of Cartesian displacements and bond angles. However, a simple limiting case occurs when the central atom is much heavier than the end atoms, a close enough approximation to the H_2O molecule to afford a qualitative understanding of the vibrational modes in that molecule. In this limiting case, the center of mass is fixed on the central atom and the normal coordinates become the same as the symmetry coordinates shown in figure 6.3 if the motion of the central atom vanishes. Then the interatomic bond distances are

$$q_1 = S_1 + S_3 \tag{6.41a}$$

$$q_2 = S_1 - S_3 \tag{6.41b}$$

and the change in bond angle is

$$\phi = \frac{2}{d}S_2 \tag{6.41c}$$

The kinetic energy expressed in these coordinates is

$$T = \frac{m_1}{2}\left[(\dot{S}_1 + \dot{S}_3)^2 + \dot{S}_2{}^2\right] + \frac{m_1}{2}\left[(\dot{S}_1 - \dot{S}_3)^2 + \dot{S}_2{}^2\right]$$

$$= m_1\left[\dot{S}_1{}^2 + \dot{S}_2{}^2 + \dot{S}_3{}^2\right] \tag{6.42}$$

while the potential energy in equation (6.29) takes the form

$$V = \frac{k}{2}\left[(S_1 + S_3)^2 + (S_1 - S_3)^2\right] + \delta(S_1 + S_3)(S_1 - S_3) + 2\varepsilon S_2{}^2$$

$$= (k + \delta)S_1{}^2 + 2\varepsilon S_2{}^2 + (k - \delta)S_3{}^2 \tag{6.43}$$

The approximate normal mode frequencies are immediately apparent from inspection of equations (6.42) and (6.43):

$$\omega_1{}^2 \simeq \frac{b_{11}}{a_{11}} = \frac{k + \delta}{m_1} \tag{6.44a}$$

$$\omega_2{}^2 \simeq \frac{b_{22}}{a_{22}} = \frac{2\varepsilon}{m_1} \tag{6.44b}$$

$$\omega_3{}^2 \simeq \frac{b_{33}}{a_{33}} = \frac{k - \delta}{m_1} \tag{6.44c}$$

and the approximate force constants in terms of the observed frequencies are

$$k \simeq \frac{m_1}{2}(\omega_1{}^2 + \omega_3{}^2) \tag{6.45a}$$

$$\delta \simeq \frac{m_1}{2}(\omega_1{}^2 - \omega_3{}^2) \tag{6.45b}$$

$$\varepsilon \simeq \frac{m_1}{2}\omega_2{}^2 \tag{6.45c}$$

These results are the same as obtained from equations (6.36), (6.39), and (6.40) when the mass ratio m_1/m_2 is allowed to vanish; in this case, the bond angle α is irrelevant. Results are insensitive to bond angle whenever the ratio m_1/m_2 is small.

Problem 6.6: Show that the approximate force constants for H_2O, obtained by treating the central O atom as infinitely heavy, are

$k = 8.08\times10^5$ dyne-cm

$\delta = -2.30\times10^4$ dyne-cm

$\varepsilon = 7.48\times10^4$ dyne-cm

Observe that the results obtained by this approximation are only about 5 percent different for k and ε from the results obtained in problem 6.4, but the coupling constant δ is about twice as large as given by the more accurate treatment.

6.8 DEGENERATE VIBRATIONAL MODES

The linear triatomic molecule has two equivalent modes of bending vibrational motion which have equal energy levels, so these modes are doubly degenerate. The total vibrational energy of the molecule is

$$\frac{E}{\hbar} = \omega_1\left(v_1 + \frac{1}{2}\right) + \omega_2\left(v_{2a} + \frac{1}{2}\right) + \omega_2\left(v_{2b} + \frac{1}{2}\right) + \omega_3\left(v_3 + \frac{1}{2}\right) \tag{6.46}$$

and the total wave function is the product of normal mode wave functions

$$\psi = N\, e^{-(y_1^2 + y_{2a}^2 + y_{2b}^2 + y_3^2)/2} H_{v_1}(y_1) H_{v_{2a}}(y_{2a}) H_{v_{2b}}(y_{2b}) H_{v_3}(y_3) \tag{6.47}$$

where v_1, v_{2a}, v_{2b}, and v_3 are the quantum numbers for the four normal mode vibrations and N is the normalization constant (the product of four separate normalization factors given by eq. (5.19a)) and y_i are dimensionless normal coordinates used in problem 6.1:

$$y_i = \left(\frac{\mu_i \omega_i}{\hbar}\right)^{1/2} S_i \tag{6.48}$$

The modes with equal circular frequencies ω_2 can be combined to yield

$$\frac{E}{\hbar} = \ldots \omega_2(v_2 + 1) + \ldots \tag{6.49}$$

where v_2 represents the total quantum number

$$v_2 = v_{2a} + v_{2b} \tag{6.50}$$

Note that the ground-state energy is $\hbar\omega_2$ for these modes. The degeneracy of the state with quantum number v_2 is

$$g(v_2) = v_2 + 1 \tag{6.51}$$

corresponding to the number of different ways v_{2a} and v_{2b} can be selected to add up to v_2

$$v_{2a} = 0, \quad 1, \quad 2, \ldots, v_2$$

$$v_{2b} = v_2, \; v_2 - 1, \; v_2 - 2, \ldots, 0$$

Problem 6.7: Show that the partition function given by the product of two identical simple harmonic oscillator partition functions is the same as the partition function for an oscillator that has a degeneracy $(v + 1)$ for each level. Use the ground state as the zero reference energy level,

$$Q = \left[\sum_{v=0}^{\infty} e^{-v(\hbar\omega/kT)}\right]^2 = \sum_{v=0}^{\infty} (v + 1)e^{-v(\hbar\omega/kT)} = \left(1 - e^{-\hbar\omega/kT}\right)^{-2}$$

In the general polyatomic molecule, several modes of vibration may be degenerate and the energy can then be expressed as

$$\frac{E}{\hbar} = \ . \ . \ . \ \omega_i\left(v_i + \frac{n_i}{2}\right) + \ . \ . \ . \tag{6.49a}$$

where n_i is the number of degenerate modes with the same circular frequency ω_i. The total quantum number v_i represents the sum of n_i vibrational quantum numbers

$$v_i = \sum_{j=0}^{n_i} v_{ij} \tag{6.50a}$$

and the degeneracy is the number of ways n_i positive numbers can be chosen to add up to v_i:

$$g(v_i) = \frac{(v_i + n_i - 1)!}{v_i!\,(n_i - 1)!} \tag{6.51a}$$

Complete decoupling between vibrational modes occurs only when the potential is purely quadratic in form as in equation (6.5). Actually, some anharmonicity is always present, corresponding to finite third- or higher-order partial derivatives in the potential function. Then cross-coupling terms appear which cannot be made to vanish in both potential and kinetic energy expressions by any linear transformation of coordinates. This coupling splits the energy states, and the level of degeneracy g appears as g separate lines. For example, consider two equivalent oscillators of mass m and resonant circular frequency ω which are coupled. The potential is expressed as

$$V = \frac{m\omega^2 x_1{}^2}{2} + \frac{m\omega^2 x_2{}^2}{2} + m\varepsilon^2 x_1 x_2 \tag{6.52a}$$

where $m\varepsilon^2$ is a force constant representing the effect of the anharmonic perturbation coupling. In normal coordinates,

$$S_1 = \frac{1}{\sqrt{2}}\,(x_1 + x_2) \tag{6.53a}$$

$$S_2 = \frac{1}{\sqrt{2}}\,(x_1 - x_2) \tag{6.53b}$$

This potential becomes

$$V = \frac{m}{2}(\omega^2 + \varepsilon^2)S_1{}^2 + \frac{m}{2}(\omega^2 - \varepsilon^2)S_2{}^2 \tag{6.52b}$$

while the kinetic energy is

$$T = \frac{m}{2}(\dot{S}_1{}^2 + \dot{S}_2{}^2) \tag{6.54}$$

Solutions to the equations of motion are

$$S_1 = S_{10}\, e^{i(\omega^2+\varepsilon^2)^{1/2}t} \tag{6.55a}$$

$$S_2 = S_{20}\, e^{i(\omega^2-\varepsilon^2)^{1/2}t} \tag{6.55b}$$

For these normal coordinates, the system is in steady state, with each normal mode oscillating independently. In terms of the individual oscillator displacements x_1 and x_2, the system appears to be in resonance, with a transient surging of vibrational energy back and forth from one oscillator to the other:

$$x_1 = \frac{1}{\sqrt{2}}\left[S_{10}\, e^{i(\omega^2+\varepsilon^2)^{1/2}t} + S_{20}\, e^{i(\omega^2-\varepsilon^2)^{1/2}t}\right] \tag{6.56a}$$

$$x_2 = \frac{1}{\sqrt{2}}\left[S_{10}\, e^{i(\omega^2+\varepsilon^2)^{1/2}t} - S_{20}\, e^{i(\omega^2-\varepsilon^2)^{1/2}t}\right] \tag{6.56b}$$

However, the transient appearance of the resonance phenomena is merely an artifact introduced by viewing the system in other than normal coordinates. The total system is in a dynamic steady state, which becomes evident when the system is viewed in normal coordinates.

In quantum mechanics, the coupled system has the quantized energy levels

$$E = \left(v_1 + \frac{1}{2}\right)\hbar(\omega^2 + \varepsilon^2)^{1/2} + \left(v_2 + \frac{1}{2}\right)\hbar(\omega^2 - \varepsilon^2)^{1/2} \tag{6.57}$$

where v_1 and v_2 are quantum numbers for the two unperturbed normal modes. For small coupling, $\varepsilon \ll \omega$, this may be expanded to

$$E = \hbar\omega\left[(v + 1) + l\,\frac{\varepsilon^2}{2\omega^2} + \ldots\right] \tag{6.58}$$

where the total quantum number $v = (v_1 + v_2)$ and $l = (v_1 - v_2)$ or $(v - 2v_2)$. There are $v + 1$ distinct levels symmetrically placed about the central energy level $(v+1)\hbar\omega$ associated with the different values of $v_1 - v_2$, both positive and negative, which the difference between two integers that sum to v can take. The spacing between levels $\hbar\omega(\varepsilon^2/\omega^2)$ is proportional to the strength of the coupling force constant ε^2. The splitting and degeneracy of levels for a doubly degenerate set of vibrational modes is illustrated in figure 6.4. Usually, this splitting is very small for the lower vibrational levels, but the anharmonic effects can become more pronounced in the upper levels.

The vibrational state of triatomic molecules, whether linear or nonlinear, is, by convention, designated by a brace of three numbers (v_1, v_2, v_3), where v_1 is the vibrational quantum number associated with the symmetric stretch mode, v_2 is the quantum number associated with the bending modes, and v_3 is the quantum number associated with the asymmetric stretch mode. If the molecule is nonlinear, only one bending mode in the plane of the three atoms is involved. However, if the molecule is linear, the bending modes are doubly degenerate and v_2 then designates the total quantum number $v_{2a} + v_{2b}$ and is given a supercript $|l|$ that is the absolute magnitude of the difference $(v_{2a} - v_{2b})$. That is, the state is designated by the brace $(v_1, v_2^{|l|}, v_3)$. For example, the $(1, 3^1, 0)$ state of CO_2 indicates that one quantum of vibrational energy is excited in the symmetric stretch mode, three quanta of energy are excited in the bending modes with two quanta in one degenerate bending mode and one in the other, while the asymmetric stretch mode is in the ground state. Another state with nearly the same energy is $(1, 3^3, 0)$; in this case, all three quanta in the bending modes are in one of the degenerate modes while the other mode is in the ground state. The phase angles of classical motion are such that the 3^1 state has one quantum unit while the 3^3 state has three quantum units of angular momentum in the bending motion.

6.9 FERMI RESONANCE BETWEEN STATES

States that are not degenerate will also be coupled to one another by anharmonic terms in the potential. The wave function can then be expressed as a series expansion in the orthonormal set of wave functions $\psi_k{}^o$ as

$$\psi_n = \sum_{k=0}^{\infty} a_{nk}\psi_k{}^o \tag{6.59}$$

which are first-order solutions in terms of normal coordinates y_i obtained when the anharmonic terms are neglected:

$$\psi_k{}^o(y_1, y_2, y_3, \ldots, y_n) = u_1(y_1)u_2(y_2)\ldots u_n(y_n) \tag{6.60}$$

and the $u_i(y_i)$ terms are the single-mode harmonic oscillator wave functions. In actual practice, only those states that are very close to one another in energy are effectively coupled, and even then only if the wave functions have like symmetry properties. The coupling effect is called Fermi resonance, in

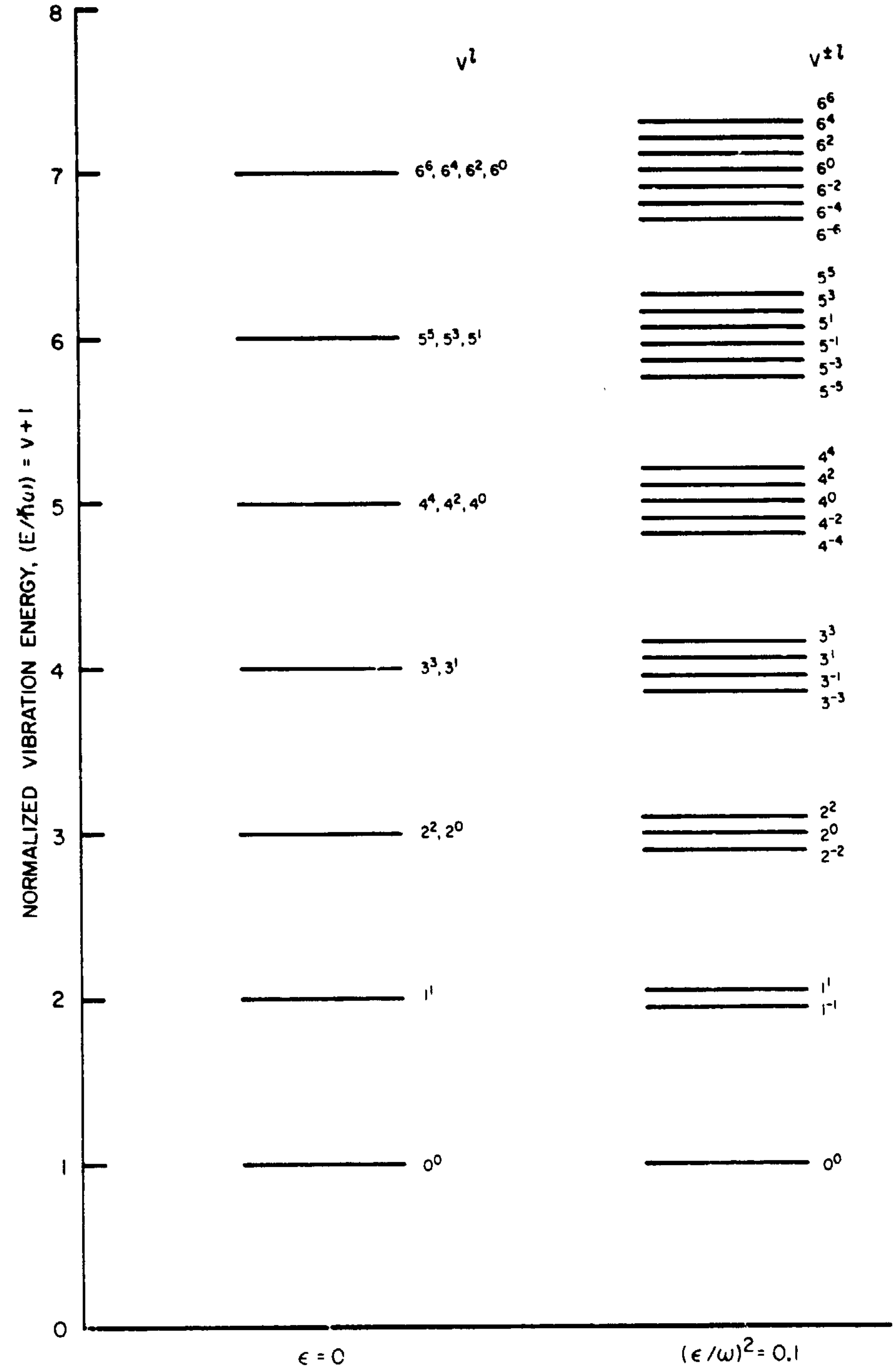

Figure 6.4.- Energy levels for a doubly degenerate set of vibrational modes.

deference to the analogy with nearly resonant classical oscillators, but the word resonance should not be construed to imply a time-dependent state. The coupled states are in steady state at steady-state perturbed energy levels and with steady-state mixed wave functions. Often, only two levels are involved in any one set of coupled states. In this case, Fermi resonance can be illustrated by considering a two-state system with levels 1 and 2. The wave functions are taken to be linear combinations of the unperturbed wave functions $\psi_1{}^0$ and $\psi_2{}^0$:

$$\psi = a_1\psi_1{}^0 + a_2\psi_2{}^0 \tag{6.61}$$

with constant coefficients a_1 and a_2.

Perhaps it is appropriate at this point to note that the term "mixed" wave function denotes the approximation in which the wave function is taken to be a linear sum of "normal" wave functions as in equation (6.59) or (6.61). The coefficients may be constants, as in the steady-state problem considered here, or functions of time if the wave functions and energy levels are being determined for a time-dependent perturbation. Usually, these coefficients squared are interpreted as the probabilities that the system resides in a state represented by the corresponding normal wave function. However, note that the wave function can be expanded in *any* orthogonal set, and the coefficients squared then represent the probabilities of being in a completely different set of so-called "normal" states. For a time-dependent perturbation, the concept of normal and mixed states has more physical meaning in that the system is required to be in one of the normal states before the perturbation event, and then ends up with certain probabilities in one of the available normal states after the perturbation event. The mixed states are merely states that the system may take during the perturbation. In the present case of Fermi resonance, however, we are considering a steady-state situation in which the third- and higher-order derivatives in the potential are permanent and normal. The so-called mixed state is the normal steady state, and if we knew how to express the wave functions for these states exactly, we would describe the system in any one of these states with a single wave function with no concept of mixing whatever.

The Hamiltonian operator is now taken as the sum $\widetilde{H}_0 + \widetilde{H}'$, where $\widetilde{H}_0$ contains the dominant quadratic terms in the energy which lead to the harmonic oscillator solutions in terms of normal coordinates (eq. (6.60)), and $\widetilde{H}'$ represents a perturbation provided by the higher-order anharmonic terms in the Hamiltonian. Since $\widetilde{H}_0\psi_1{}^0 = E_1{}^0\psi_1{}^0$ and $\widetilde{H}_0\psi_2{}^0 = E_2{}^0\psi_2{}^0$, where $E_1{}^0$ and $E_2{}^0$ are the harmonic oscillator energies, the Schroedinger equation becomes

$$(\widetilde{H}_0 + \widetilde{H}')\psi = E(a_1\psi_1{}^0 + a_2\psi_2{}^0) = a_1E_1{}^0\psi_1{}^0 + a_2E_2{}^0\psi_2{}^0 + a_1\widetilde{H}'\psi_1{}^0 + a_2\widetilde{H}'\psi_2{}^0 \tag{6.62}$$

Equation (6.62) is first multiplied by $\psi_1{}^{0*}$ and integrated over all space and then again multiplied by $\psi_2{}^{0*}$ and integrated over all space to yield a set of two simultaneous equations to solve for the constants a_1 and a_2:

$$(E_1{}^0 - E)a_1 + a_1H_{11} + a_2H_{12} = 0 \tag{6.63a}$$

$$(E_2{}^0 - E)a_2 + a_1H_{21} + a_2H_{22} = 0 \tag{6.63b}$$

where the matrix elements H_{ij} are defined as

$$H_{ij} = \int \psi_i{}^{0*}\tilde{H}'\psi_j{}^0 \, d\tau \tag{6.64}$$

We need not actually solve for the constants a_1 and a_2 to obtain the allowed energy levels, for the simultaneous equations (6.63a) and (6.63b) have finite solutions if and only if the matrix equation

$$\begin{vmatrix} (E_1{}^0 + H_{11} - E) & H_{12} \\ H_{21} & (E_2{}^0 + H_{22} - E) \end{vmatrix} = 0 \tag{6.65}$$

is satisfied. The two roots of this determinant are

$$E = \frac{1}{2}\left[(E_1{}^0 + H_{11}) + (E_2{}^0 + H_{22})\right] \pm \frac{1}{2}\sqrt{\left[(E_1{}^0 + H_{11}) - (E_2{}^0 + H_{22})\right]^2 + 4H_{12}H_{21}} \tag{6.66}$$

The perturbation potential is normally dominated by the third derivative terms, so the perturbation Hamiltonian can be expressed as

$$H' = \sum_{i,j,k} \frac{1}{3!} \frac{\partial^3 V}{\partial y_i \, \partial y_j \, \partial y_k} y_i y_j y_k \tag{6.67}$$

In this case, the matrix elements H_{11} and H_{22} both contain factors of the form

$$\int y_i u_i{}^2(y_i) dy_i \quad \text{or} \quad \int y_i{}^3 u_i{}^2(y_i) dy_i$$

where the $u_i(y_i)$ terms are the single-mode harmonic oscillator wave functions specified in equation (6.60), and these factors all vanish because of symmetry. Thus H_{11} and H_{22} can be expected to be very small, depending only on fourth- and higher-order terms in the Taylor series expansion of the potential. In addition, because the perturbation involves only the coordinates and no momenta, the perturbation Hamiltonian H' contains no differential operators with the result that $H_{12} = H_{21}$. To a good approximation then, the Fermi resonant energy levels given by equation (6.66) become

$$E \approx \frac{E_1{}^0 + E_2{}^0}{2} \pm \frac{1}{2}\sqrt{(E_1{}^0 - E_2{}^0)^2 + 4H_{12}^2} \tag{6.66a}$$

If the unperturbed levels are degenerate, that is, $E_1{}^0 = E_2{}^0$, the perturbation splits the levels an equal amount higher and lower in energy:

$$E_{1,2} \simeq E_1{}^0 \pm H_{12} \tag{6.66b}$$

If the unperturbed energy levels have an energy difference small compared with the perturbation matrix element H_{12},

$$E_{1,2} \simeq \frac{E_1{}^0 + E_2{}^0}{2} \pm \frac{(E_1{}^0 - E_2{}^0)^2}{8H_{12}} \pm H_{12} \tag{6.66c}$$

and, finally, if H_{12} is small compared with the energy difference $(E_1{}^0 - E_2{}^0)$, the Fermi resonant levels become

$$E_1 \simeq E_1{}^0 + \frac{H_{12}^2}{E_1{}^0 - E_2{}^0} \tag{6.66d}$$

$$E_2 \simeq E_2{}^0 - \frac{H_{12}^2}{E_1{}^0 - E_2{}^0} \tag{6.66e}$$

In this case, the upper level is elevated in energy and the lower level is depressed by equal amounts - the same result given by small-perturbation theory (eq. (5.40)) for a two-level system.

The third derivatives of the potential are not normally known *a priori*, so the matrix elements H_{12} are evaluated by empirically fitting the results to the observed energy levels. Since these elements are normally quite small, only those levels with nearly equal energy, $E_i{}^0 \simeq E_j{}^0$, will contribute appreciably to the Fermi resonance effect and often only a two-level system needs to be considered. If more than two levels happen to have nearly equal energy, the same procedures are followed in setting up an m level system, mixing the wave functions as above, and finally one obtains an m-rank determinant in place of equation (6.65) to solve for the allowed energy levels. Not all levels of nearly equal energy exhibit Fermi resonance, however; only those having the same symmetry type will mix. If the wave functions have a different symmetry in some of the coordinates other than the vibrational coordinates (e.g., a rotational angular coordinate), the matrix elements for perturbations of the type given by equation (6.67) will all vanish. One would need to consider rotation-vibration coupling to obtain expressions for the mixing of states with different rotational symmetry. To some degree, all harmonic oscillator states of the same symmetry are mixed by anharmonic terms in the potential, and states of different symmetry are mixed by higher-order coupling terms. One should, however, keep in mind that the real states are not mixed at all - each is a pure eigenstate for the actual Hamiltonian that exists. The so-called mixing of states is an artifact produced by the choice of normal coordinates in which the motions of the system are viewed or, in other words, the choice of harmonic oscillator wave functions as an orthonormal set of functions in which to expand the actual wave function.

Fermi resonance occurs between other internal energy modes, of course, as well as the oscillator modes, such as rotational or electronic modes, whenever the energies are close and the symmetries are correct. In any case, the analysis proceeds by the same general perturbation schemes outlined above.

Problem 6.8(a). Show that if the wave functions

$$\psi_1 = a_{11}\psi_1{}^0 + a_{12}\psi_2{}^0 \tag{6.68a}$$

$$\psi_2 = a_{21}\psi_1{}^0 + a_{22}\psi_2{}^0 \tag{6.68b}$$

are orthogonal and normalized, where $\psi_1{}^0$ and $\psi_2{}^0$ are two eigenfunctions of an orthonormal set, the constant coefficients a_{ij} must be related:

$$a_{11} = \pm a_{22} \tag{6.69a}$$

$$a_{12} = \mp a_{21} \tag{6.69b}$$

(b) Consider Fermi resonance between the states $\psi_1{}^0$ and $\psi_2{}^0$ for $E_1{}^0 = E_2{}^0$ and $H_{11} = H_{22} = 0$ and show that the wave functions become

$$\psi_{1,2} \approx \frac{1}{\sqrt{2}}(\psi_1{}^0 \pm \psi_2{}^0) \tag{6.70}$$

(c) Consider Fermi resonance between the same two states for $H_{11} = H_{22} = 0$, where $H_{12} \ll E_1{}^0 - E_2{}^0$, and show that the constant coefficients may then be expressed as

$$a_{22} = a_{11} \approx 1 - \frac{H_{12}{}^2}{2(E_1{}^0 - E_2{}^0)^2} \tag{6.71a}$$

$$a_{21} = -a_{12} \approx \frac{H_{12}}{E_1{}^0 - E_2{}^0} \tag{6.71b}$$

Note that multiplying either of the wave functions in equation (6.68) by -1 yields the same solution, as indicated by the sign permutations in equation (6.69).

For CO_2, a strong resonance exists between the 10^00 level and the 02^00 level, but the 02^20 level has a different symmetry and does not couple with the 10^00 level. To conveniently examine the symmetry of such states, the bending mode wave functions next are expressed in terms of normalized polar coordinates rather than the set y_{2a} and y_{2b} used previously.

6.10 LINEAR TRIATOMIC MOLECULE BENDING MODES IN POLAR COORDINATES

The vibrational bending modes of a linear triatomic molecule were found to have the wave function

$$\psi = N_{v_1}N_{v_2}\, e^{-(y_1{}^2+y_2{}^2)/2} H_{v_1}(y_1) H_{v_2}(y_2) \tag{6.72}$$

This wave function can be expressed in terms of the polar coordinates ρ and λ, defined as

$$y_1{}^2 + y_2{}^2 = \rho^2 \tag{6.73a}$$

$$\tan \frac{y_1}{y_2} = \lambda \qquad (6.73b)$$

Schroedinger's equation in cylindrical coordinates becomes

$$\frac{\partial^2\psi}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial\psi}{\partial\rho} + \frac{1}{\rho^2}\frac{\partial^2\psi}{\partial\lambda^2} + \left(\frac{2E}{\hbar\omega} - \rho^2\right)\psi = 0 \qquad (6.74)$$

Assume the wave function is separable:

$$\psi = R(\rho)\Phi(\lambda) \qquad (6.75)$$

Substitute equation (6.75) into (6.74) and multiply by $\rho^2/R\Phi$:

$$\frac{\rho^2}{R}\frac{d^2R}{d\rho^2} + \frac{\rho}{R}\frac{dR}{d\rho} + \left(\frac{2E}{\hbar\omega} - \rho^2\right)\rho^2 + \frac{1}{\Phi}\frac{d^2\Phi}{d\lambda^2} = 0 \qquad (6.76)$$

The functions of ρ and λ in equation (6.76) must each be constant to satisfy the equation. Let

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\lambda^2} = -l^2 \qquad (6.77)$$

Then the normalized solution for Φ is

$$\Phi = \frac{e^{\pm il\lambda}}{\sqrt{2\pi}} \qquad (6.78)$$

The quantum number l must obviously be an integer if the wave function is to be single-valued. Only positive integers need be considered since negative values have been allowed for in the exponent. The remaining wave function for R is

$$\rho^2\frac{d^2R}{d\rho^2} + \rho\frac{dR}{d\rho} + \left(\frac{2E}{\hbar\omega} - \frac{l^2}{\rho^2} - \rho^2\right)\rho^2 R = 0 \qquad (6.79)$$

At $\rho \to \infty$, the solution for R obviously varies as $e^{-\rho^2/2}$, and the singularity at the origin can be removed by factoring out ρ^l. Let $x = \rho^2$, then

$$R(\rho) = e^{-\rho^2/2}\rho^l L(\rho^2) = e^{-x/2}x^{l/2}L(x) \qquad (6.80)$$

Substitute equation (6.80) into (6.79) and obtain the differential equation for the function $L(x)$:

$$x \frac{d^2L}{dx^2} + (l + 1 - x) \frac{dL}{dx} + \left(\frac{E}{2\hbar\omega} - \frac{1}{2} - \frac{l}{2}\right) L = 0 \tag{6.81}$$

This is Laguerre's equation again, and a finite polynomial solution exists when the last factor is

$$\left(\frac{E}{2\hbar\omega} - \frac{1}{2} - \frac{l}{2}\right) L = (n - l)L \tag{6.82}$$

where n is any positive integer from l to ∞. These solutions are the associated Laguerre polynomials:

$$L = L_n{}^l(x) \tag{6.83}$$

The Laguerre polynomials are defined by

$$L_n(x) = e^x \frac{d^n}{dx^n} (e^{-x} x^n) \tag{6.83a}$$

and the associated Laguerre polynomials by

$$L_n{}^l(x) = \frac{d^l}{dx^l} L_n(x) \tag{6.83b}$$

The first few Laguerre and associated Laguerre polynomials are

$$L_0(x) = 1$$

$$L_1(x) = -(x - 1)$$

$$L_1{}^1(x) = -1$$

$$L_2(x) = x^2 - 4x + 2$$

$$L_2{}^1(x) = 2x - 4$$

$$L_2{}^2(x) = 2$$

$$L_3(x) = -(x^3 - 9x^2 + 18x - 6)$$

$$L_3{}^1(x) = -(3x^2 - 18x + 18)$$

$$L_3{}^2(x) = -(6x - 18)$$

$$L_3{}^3(x) = -6$$

The list may be extended by means of the recursion relation:

$$L_{n+1}(x) + (x - 1 - 2n)L_n(x) + n^2 L_{n-1}(x) = 0 \tag{6.83c}$$

From equation (6.82), the allowed energy levels are

$$\frac{E}{\hbar\omega} = (2n - l + 1) = v + 1 \tag{6.84}$$

where v is the total quantum number $2n - l$. This expression is the same as found in equation (6.49) for the energy levels of two degenerate modes of vibration. The total wave function in polar coordinates becomes

$$\psi_{vl} = R_v \Phi_l = N_v\ e^{-\rho^2/2} \rho^l L^l_{(v+l)/2}(\rho^2) e^{\pm il\lambda} \tag{6.85}$$

where ρ^2 is a dimensionless normal coordinate that may be related to the bending angles ϕ_a and ϕ_b by

$$\rho^2 = \frac{\omega_2 a_{22}}{\hbar} (S^2_{2a} + S^2_{2b}) \tag{6.86a}$$

For the particular set of normal coordinates chosen (see fig. 6.2), this becomes

$$\rho^2 = \frac{\omega_2 m_1}{\hbar} \left(1 + \frac{2m_1}{m_2}\right) (S^2_{2a} + S^2_{2b}) = \frac{\omega_2 d^2 ({\phi_a}^2 + {\phi_b}^2)}{4\hbar \left(\frac{1}{m_1} + \frac{2}{m_2}\right)} \tag{6.86b}$$

The integer $(v + l)/2$ must be equal to or greater than the integer l if the Laguerre equation is to have a finite polynomial solution. Thus, there are $(v + 1)$ different wave functions that correspond to the values

$l = 0, 2, 4, \ldots, v$ if v is even

$l = 1, 3, 5, \ldots, v$ if v is odd

and that allow for both positive and negative exponents in the factor $e^{\pm il\lambda}$ except when $l = 0$.

Problem 6.9: Use the moment-generating functions for the associated Laguerre polynomials to evaluate the normalization constant required for the wave function in equation (6.85):

$$U_s(x,u) = \sum_{r=s}^{\infty} \frac{L^s_r(x) u^r}{r!} = (-1)^s \frac{e^{-xu/(1-u)} u^s}{(1 - u)^{s+1}}$$

$$V_s(x,y) = \sum_{t=s}^{\infty} \frac{L^s_t(x) y^t}{t!} = (-1)^s \frac{e^{-xy/(1-y)} y^s}{(1 - y)^{s+1}}$$

Integrate the product $e^{-x}x^{s}U_{s}V_{s}$ over all x from 0 to ∞ to show that

$$\sum_{r,t=s}^{\infty}\sum \frac{u^{r}y^{t}}{r!t!}\int_{0}^{\infty} e^{-x}x^{s}L_{r}^{s}L_{t}^{s}\,dx = \frac{(uy)^{s}}{(1-u)^{s+1}(1-y)^{s+1}}\int_{0}^{\infty} x^{s}\,e^{-x(1-uy)/(1-u)(1-y)}\,dx$$

$$= \sum_{k=0}^{\infty} \frac{(s+k)!}{k!}(uy)^{s+k}$$

Isolate those terms where $r = t = (v + l)/2$ and $s = l$ and, by comparing coefficients, show that

$$\int_{0}^{\infty} e^{-x}x^{l}\left[L_{(v+l)/2}^{l}\right]^{2} dx = \frac{\left[\left(\frac{v+l}{2}\right)!\right]^{3}}{\left(\frac{v-l}{2}\right)!} \tag{6.87}$$

Show that the normalization constant in equation (6.85) is given by

$$N_{vl}^{2} = \frac{\mu\omega}{\pi\hbar}\,\frac{\left(\frac{v-l}{2}\right)!}{\left[\left(\frac{v+l}{2}\right)!\right]^{3}} \tag{6.88}$$

Classically, the degenerate normal mode vibrations can be coupled in any arbitrary phase and the coupled motion follows an elliptic path in space which will have angular momentum of any value from zero up to the maximum, where the angular momentum energy equals the total vibrational energy. In this state, the linear molecule is rolling in a permanently bent configuration such that the centrifugal forces balance the restoring forces. Quantum mechanically, only those phase couplings are allowed where the angular momentum takes integral values of $\hbar$. The total energy is not changed by the different values of angular momentum if the small anharmonic effects be neglected - which actually do split the degenerate levels slightly. The increase in rotational energy as l increases is balanced by a decrease in kinetic and potential energies associated with changes in the bending angle. The doubly-degenerate modes are designated by the index v^{l}, where v is the total vibrational quantum number giving the total energy and l is the absolute magnitude of the rotational quantum number which, to the harmonic potential approximation, does not affect that total energy, but which establishes the symmetry properties of the wave function. As previously discussed, the integer l is the absolute magnitude of the difference between the quantum numbers of the individual modes $|v_2 - v_1|$. When $v_2 = v_1 = v/2$, the motions are in phase and the angular momentum is zero. When v_1 or $v_2 = v$, the motion is 90° out of phase with the ground-state motion in the other mode and the angular momentum is a maximum. The splitting of levels associated with a coupling frequency ε is shown for the different levels in figure 6.4.

We can now see how the symmetry properties of the wave function affect the Fermi resonance coupling. The anharmonic terms are expected to involve the bending angles and associated displacements, but because of symmetry they cannot involve the angular position λ. Thus, only those states can couple where both values of l are equal; otherwise, the matrix elements U_{12} (see eq. (5.33)) will vanish.

The CO_2 molecule is a good example of the above. The bending-mode frequency (ω_2 = 667.5 cm^{-1}) is very nearly half the symmetric stretch-mode frequency (ω_1 = 1337 cm^{-1}). Thus, the unperturbed energy levels (0, 2^0, 0) and (0, 2^2, 0) (1335 cm^{-1}) are only about two wave numbers distant from energy level (1, 0^0, 0), and the first requirement for Fermi resonance is satisfied, namely, that the unperturbed energy levels are close. The 0, 2^2, 0 state will not couple with the 1, 0^0, 0 mode, however, as the matrix element includes a factor that vanishes:

$$\int_0^{2\pi} e^{\pm 2i\lambda}\, d\lambda = 0$$

Indeed, the 0, 2^2, 0 state is observed to lie at almost exactly its unperturbed value. However, the energy of the 0, 2^0, 0 state is depressed to 1284 cm^{-1} while the 1, 0^0, 0 state is elevated to 1388 cm^{-1} by Fermi resonance between the two states. These are nearly symmetrically placed about the unperturbed value as predicted by theory. A perturbation matrix element U_{12} = 52 cm^{-1} is required to explain these results.

Some higher vibrational levels of CO_2 will also be in Fermi resonance with one another, for example, the 0, 3^1, 0 and 1, 1^1, 0 levels. The next set of levels with close-lying energy and the same symmetry are the 0, 4^0, 0; 1, 2^0, 0; and 2, 0^0, 0 levels. In this case, three levels are involved and the perturbation treatment would need to be expanded to include three levels.

The linear triatomic molecule C_3 is considered next because it is a good example of the principles discussed above; in addition, it exhibits some abnormally large deviations from the usual normal-mode approximation and affords a chance to introduce some of the techniques useful in analyzing such deviations.

6.11 LARGE-AMPLITUDE BENDING OF C_3

The bending motions of most triatomic molecules can be adequately treated as small-amplitude, normal-mode displacements with higher-order corrections provided by small-perturbation treatment. The linear triatomic C_3 molecule, which appears in the ablation of graphite heat shields and in gaseous products of hydrocarbon combustion, is an interesting exception. This linear molecule has a very low bending frequency (refs. 3-5), about 63 cm^{-1}, and maximum total bending angles are large (ref. 6), the order of 60°. With such large-amplitude bending, one naturally expects deviations from normal mode models. Gausset et al (ref. 4) and Merer (ref. 7) observe a decrease in the moment of inertia as the bending quantum number increases, which indicates that the end atoms are pulled inward as the bending angle increases and that the Hamiltonian should include terms for the curvilinear motions of the atomic nuclei. Since C_3 stretch vibrations have respectably large frequencies (ref. 8) that indicate a stiff bond (1225 cm^{-1} for symmetric stretch and 2030 cm^{-1} for asymmetric stretch), these vibrations can be treated to a reasonable approximation as completely decoupled modes. This permits us to concentrate on a simple model for the Hamiltonian that isolates the effects of large-amplitude bending on the rotational constant and on the bending energy levels so that these effects can be readily visualized.

Figure 6.5 shows the geometry of the bending molecule. The parameter δ accounts for the curvilinear motion of the end atoms by defining point A a constant distance d from the end atoms, where d is the interatomic spacing at zero bending. If $\delta = 0$, the end atoms move rectilinearly along normal mode coordinates; if $\delta = 1/3$, the end atoms move along circular arcs a fixed distance d from the center of mass; if $\delta = 1$, the atoms move along arcs a fixed distance d from the central atom. Generally, a variable δ is required to fit the observed variation in the moment of inertia of the molecule exactly, but a constant value is found to reproduce the observed moment of inertia for C_3 within 1 percent, which is considered sufficient for present purposes.

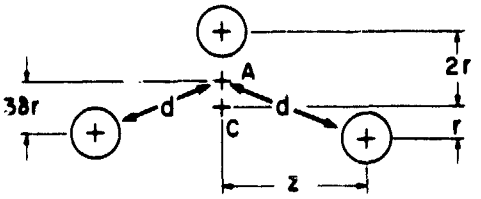

Figure 6.5.- Coordinates for linear triatomic molecule Y-Y-Y (C, center of mass; A, locus of points a fixed distance d from the end atoms during bending).

The cylindrical coordinates of the central atom (fig. 6.5) are $2r$, 0, and ϕ; the coordinates of the end atoms are r, $\pm z$, and $\phi + \pi$. The axial displacement z is

$$z = (d^2 - 9\delta^2 r^2)^{1/2} \tag{6.89}$$

and the z component of velocity can be expressed as

$$\dot{z}^2 = 3zg(r)\dot{r}^2 \tag{6.90}$$

where the function $g(r)$ is defined as

$$g(r) = \frac{27\delta^4 r^2}{d^2 - 9\delta^2 r^2}\left(1 + \frac{r}{\delta}\frac{d\delta}{\partial r}\right)^2 \tag{6.91}$$

Accordingly, the kinetic energy can be expressed as

$$T = 3m[\dot{r}^2(1 + g) + r^2\dot{\phi}^2] \tag{6.92}$$

where m is the mass of a single atom. The momenta conjugate to the r and ϕ coordinates are

$$p_r = \frac{\partial T}{\partial \dot{r}} = 6m\dot{r}(1 + g) \tag{6.93a}$$

$$p_\phi = \frac{\partial T}{\partial \dot{\phi}} = 6mr^2\dot{\phi} \tag{6.93b}$$

The Hamiltonian is the sum of the potential and kinetic energies when these are expressed in terms of coordinates and their conjugate momenta:

C-3

$$H = \frac{p_r^2}{2\mu(1 + g)} + \frac{p_\phi^2}{2\mu r^2} + V(r) \tag{6.94}$$

The reduced mass μ equals $6m$ in the present coordinate system. Note the g is a positive quantity, equation (6.91), and the effect of bending is to increase the effective reduced mass to $\mu(1 + g)$ so far as the radial coordinate motion is concerned. Accordingly, the energy eigenvalues are expected to be less than the simple harmonic oscillator eigenvalues.

The potential might be expressed in terms of arc distance or the z coordinate, but these are expressible as functions of r alone by means of the parameter δ. The potential is accordingly considered as the sum of a zeroth-order term $V^0(r)$ and a perturbation $V^1(r)$, so the Hamiltonian may be expressed as

$$H = \left(\frac{p_r^2}{2\mu} + \frac{p_\phi^2}{2\mu r^2} + V^0\right) + \left(f\,\frac{p_r^2}{2\mu} + V^1\right) \tag{6.95}$$

where the function f is the negative quantity

$$f = \frac{-g}{1 + g} \tag{6.96}$$

The Hermitian operator for the first bracket in equation (6.95) is the usual zeroth-order Hamiltonian operator in cylindrical coordinates,

$$\tilde{H}^0 = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}\right) + V^0 \tag{6.97}$$

while the Hermitian operator for the second bracket, as shown in appendix 6-A, is

$$\tilde{H}^1 = -\frac{\hbar^2}{2\mu}\left[f\,\frac{\partial^2}{\partial r^2} + \left(\frac{f}{r} + \frac{df}{dr}\right)\frac{\partial}{\partial r}\right] + V^1 \tag{6.98}$$

The potential $V^0(r)$ is chosen so that eigenfunctions ψ^0 and their corresponding eigenvalues E^0 can be found for the steady-state Schroedinger equation $\tilde{H}^0\psi^0 = E^0\psi^0$. The angular dependence of ψ^0 can be disposed of with the usual separation of variables:

$$\psi^0_{vl} = R_{vl}(r)\,\frac{e^{\pm il\phi}}{\sqrt{2\pi}} \tag{6.99}$$

where v is a total bending vibration quantum number, l is the angular momentum quantum number of bending motion, and R_{vl} is the normalized solution to

$$\frac{d^2R_{vl}}{dr^2} + \frac{1}{r}\frac{dR_{vl}}{dr} - \frac{2\mu}{\hbar^2}\left[E^0_{vl} - V^0 - \frac{l(l+1)}{r^2}\right]R_{vl} = 0 \qquad (6.100)$$

The true energy levels E_{vl} may be approximated with first-order perburbation theory by

$$E_{vl} = E^0_{vl} + U_{vl} \qquad (6.101)$$

where the matrix elements U_{vl} are defined as

$$U_{vl} = \left\langle\psi^0_{vl}\middle|\tilde{H}^1\middle|\psi^0_{vl}\right\rangle = \int_0^\infty R_{vl}(\tilde{H}^1R_{vl})r\,dr \qquad (6.102)$$

The average over all ϕ has already been performed in the last expression in equation (6.102).

The matrix elements may be further developed in a generalized form by

$$U_{vl} = -\frac{\hbar^2}{2\mu}\left[\int_0^\infty R_{vl}\frac{d^2R_{vl}}{dr^2}fr\,dr + \int_0^\infty R_{vl}\frac{dR_{vl}}{dr}\frac{d(fr)}{dr}dr\right] + \int_0^\infty R_{vl}V^1R_{vl}r\,dr \qquad (6.103)$$

The second term in equation (6.103) is integrated by parts, leading to a term that vanishes due to the boundary conditions on the wave functions R_{vl}, a term that cancels the first integral, and a final result:

$$U_{vl} = \frac{\hbar^2}{2\mu}\int_0^\infty\left(\frac{dR_{vl}}{dr}\right)^2 fr\,dr + \int_0^\infty R^2_{vl}V^1r\,dr \qquad (6.104)$$

For a constant δ, the dimensionless function f given by equation (6.96), which is needed to evaluate the matrix elements above, is

$$f = \frac{-27\delta^4(r/d)^2}{1 + (27\delta^4 - 9\delta^2)(r/d)^2} \qquad (6.105)$$

The constants δ and d are now chosen so that the averaged value of the rotational constant fits the observed variation in vibrational quantum number. For rotation about an axis perpendicular to the molecular axis of symmetry, this averaged rotational constant is

$$\bar{B} = \left\langle\frac{\hbar^2}{2I}\right\rangle = \frac{\hbar^2}{4md^2}\left\langle\frac{1}{1-(9\delta^2 - 3\sin^2\phi)(r/d)^2}\right\rangle$$

$$\approx \frac{\hbar^2}{4md^2}\left[1 + \left(9\delta^2 - \frac{3}{2}\right)\left\langle\left(\frac{r}{d}\right)^2\right\rangle + \dots\right] \qquad (6.106)$$

The last expression in equation (6.106) has been expanded to terms of order $\langle (r/d)^2 \rangle$ and averaged over all ϕ; the averaging over r remains.

The expressions derived above are general and are valid for *any* potential model. We now consider a potential that is quadratic in the bending displacement with a small quartic anharmonic term:

$$V_0 = \frac{\hbar\omega\rho^2}{2} \; ; \qquad V^1 = \varepsilon\rho^4 \tag{6.107}$$

where ρ is the normal bending coordinate

$$\rho = \left(\frac{\mu\omega}{\hbar}\right)^{1/2} r \tag{6.108}$$

and $\hbar\omega$ and ε are constants to be fitted to the observed energy levels. Because of the symmetry of the molecule, the potential cannot have terms that vary as an odd power of r. The first-order solutions are just the normalized harmonic oscillator solution in equation (6.85) with the eigenvalues given by equation (6.84). The average value of $\langle (r/d)^2 \rangle$ needed to fit equation (6.106) to the rotational constant is obtained to a first approximation using these first-order wave functions:

$$\left\langle \left(\frac{r}{d}\right)^2 \right\rangle = \frac{2\hbar}{\mu\omega d^2} \frac{\left(\frac{v - l}{2}\right)!}{\left[\left(\frac{v + l}{2}\right)!\right]^3} \int_0^\infty e^{-\rho^2} \rho^{2l} \left[L^l_{(v+l)/2}(\rho^2)\right]^2 \rho^3 \, d\rho$$

$$= \frac{\hbar}{\mu\omega d^2} (v + 1) \tag{6.109}$$

Problem 6.10: Use the moment-generating functions for the associated Laguerre polynomials from problem 6.9 to show that

$$\frac{(n - l)!}{n!^3} \int_0^\infty e^{-x} x^{l+1} \left[L^l_n(x)\right]^2 dx = (2n - l + 1)$$

and derive the value of $\langle (r/d)^2 \rangle$ given by equation (6.109).

Further show, by the same method, that

$$\frac{(n - l)!}{n!^3} \int_0^\infty e^{-x} x^{l+2} \left[L^l_n(x)\right]^2 dx = \frac{3}{2} \left[(2n - l + 1)^2 - \left(\frac{l^2 - 1}{2}\right)\right]$$

The expression for the rotational constant obtained from equations (6.106) and (6.109) is

$$\overline{B} = \frac{\hbar^2}{4md^2} \left[1 + \left(9\delta^2 - \frac{3}{2}\right)\left(\frac{\hbar}{\mu\omega d^2}\right) (v + 1) + . . . \right] \tag{6.110}$$

A relation of this functional form which fits the rotational constants measured (refs. 4 and 7) for the $v = 0$ to 6 states within 0.6 percent is

$$\overline{B} = 0.4244[1 + 0.01982(v + 1)]\text{cm}^{-1} \tag{6.111}$$

and the value of the bond length deduced by equating $\hbar^2/4md^2$ with $0.4244\ \text{cm}^{-1}$ is $d = 1.287$ Å. The value of $\omega/2\pi c$ which best fits the harmonic oscillator model of C_3 to the lowest vibrational energy levels (ref. 4) is $63.1\ \text{cm}^{-1}$ and, for this fundamental frequency, $\delta = 0.8112$ fits the harmonic oscillator model of C_3 (eq. (6.110)) to the observed rotational constants as shown in figure 6.6. An even closer fit can be obtained by retaining higher-order terms in the expansion of $\overline{B}$ and δ, but the above model suffices to show the principal effects of large-amplitude bending in C_3. The fact that δ is slightly less than unity shows that the equilibrium interatomic distance stretches to values larger than d as the bending angle increases.

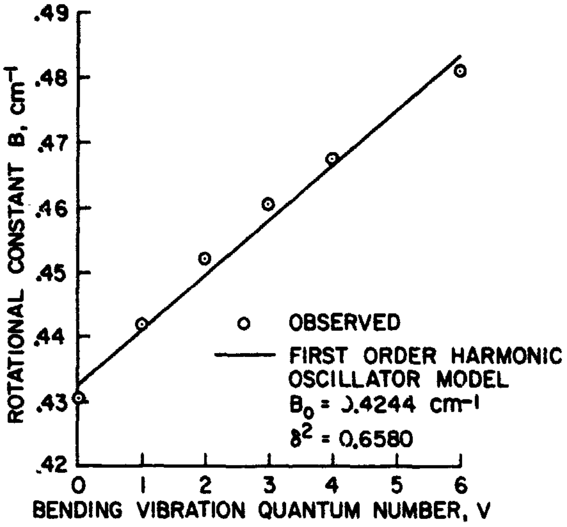

Figure 6.6.- Comparison between observed rotational constants for C_3 and the fit deduced for the harmonic oscillator model.

With the value of δ determined approximately, now calculate the perturbation matrix elements from equation (6.104). In terms of the variable $x = \rho^2 = \mu\omega r^2/\hbar$, these elements may be expressed as

$$\frac{U_{vl}}{\hbar\omega} = 2\int_0^\infty \left(\frac{dR_{vl}}{dx}\right)^2 f(x)x\ dx + \varepsilon\int_0^\infty R_{vl}^2 x^2\ dx \tag{6.112}$$

where for $d = 1.287$ Å, $\omega/2\pi c = 63.1\ \text{cm}^{-1}$, and $\delta = 0.8112$, the dimensionless function $f(x)$ is given by

$$f(x) = -\frac{0.05243x}{1 + 0.02587x} \tag{6.113}$$

and the normalized radial parts of the wave functions are

$$R_{vl} = \frac{\left[\left(\frac{v - l}{2}\right)!\right]^{1/2}}{\left[\left(\frac{v + l}{2}\right)!\right]^{3/2}} e^{-x} x^{l/2} L^l_{(v+l)/2}(x) \tag{6.114}$$

The first integral in equation (6.112) is calculated numerically. The second may be obtained analytically, according to the result obtained in problem (6.10):

$$\varepsilon \int_0^\infty R_{vl}^2 x^2 \, dx = \frac{3\varepsilon}{2} \left[(v + 1)^2 - \left(\frac{l^2 - 1}{2} \right) \right] \tag{6.115}$$

The results are shown in table 6.1 in units of $\hbar\omega$. In the column headed $(E_{vl}^0 + U_{vl})/\hbar\omega$, the first number is just $(v + 1)$, or the unperturbed harmonic oscillator energy; the second number is the first-order correction for curvilinear bending, or the first integral in equation (6.112); the final number is the first-order correction for the quartic potential term, or equation (6.115).

TABLE 6.1.- BENDING VIBRATIONAL ENERGY LEVELS FOR HARMONIC OSCILLATOR MODEL OF C_3 WITH FIRST-ORDER PERTURBATION CORRECTION FOR CURVILINEAR BENDING MOTION AND A QUARTIC PERTURBATION POTENTIAL

State, v^l	$(E_{vl}^0 + U_{vl})/\hbar\omega$	Curvilinear bending correction, percent
0^0	1.000 - 0.049 + 2ε	-4.9
1^1	2.000 - 0.070 + 6ε	-3.5
2^2	3.000 - 0.091 + 12ε	-3.0
2^0	3.000 - 0.140 + 14ε	-4.7
3^3	4.000 - 0.111 + 20ε	-2.8
3^1	4.000 - 0.207 + 24ε	-5.2
4^4	5.000 - 0.130 + 30ε	-2.6
4^2	5.000 - 0.271 + 36ε	-5.4
4^0	5.000 - 0.317 + 38ε	-6.3
5^5	6.000 - 0.148 + 42ε	-2.5
5^3	6.000 - 0.332 + 50ε	-5.5
5^1	6.000 - 0.423 + 54ε	-7.1
6^6	7.000 - 0.166 + 56ε	-2.4
6^4	7.000 - 0.390 + 66ε	-5.6
6^2	7.000 - 0.525 + 72ε	-7.7
6^0	7.000 - 0.570 + 74ε	-8.1

The effect of curvilinear motion during bending is to remove the degeneracy of states having different angular momentum, with decreases in vibrational energy between about 3 to 8 percent for the first six levels (as listed in the last column of table 6.1). The largest decreases occur for states with minimum angular momentum, $l = 0$ or 1. For these states, the classical motion is predominantly bending in a single plane and the kinetic energy associated with the z-direction velocities is maximized, leading to a maximum value of g or of the effective reduced mass. The smaller decreases occur in the upper levels with maximum angular momentum, $l = v$. For these states, the classical motion is predominantly the rolling motion of a continuously bent configuration in which the z-direction velocities are minimized.

The effects of both the curvilinear bending and a steeper than quadratic potential are needed to reproduce the observed energy levels for C_3. The splitting of energy levels and the convergence at higher quantum numbers produced by curvilinear motion alone is actually the reverse of that observed. On the other hand, the quartic perturbation effect alone produced a much larger splitting of angular momentum states than observed. The combination of the two effects results in a pattern of energy levels very similar to those observed. Figure 6.7 compares experimental energy levels and the first-order perturbation harmonic oscillator solutions of table 6.1 when $\hbar\omega$ = 56.7 cm^{-1} and ε = 0.036. One might reiterate the calculation of matrix elements using this new value of $\hbar\omega$, but the function $f(x)$ is not sensitive to the exact value of $\hbar\omega$, so the results should not be changed greatly.

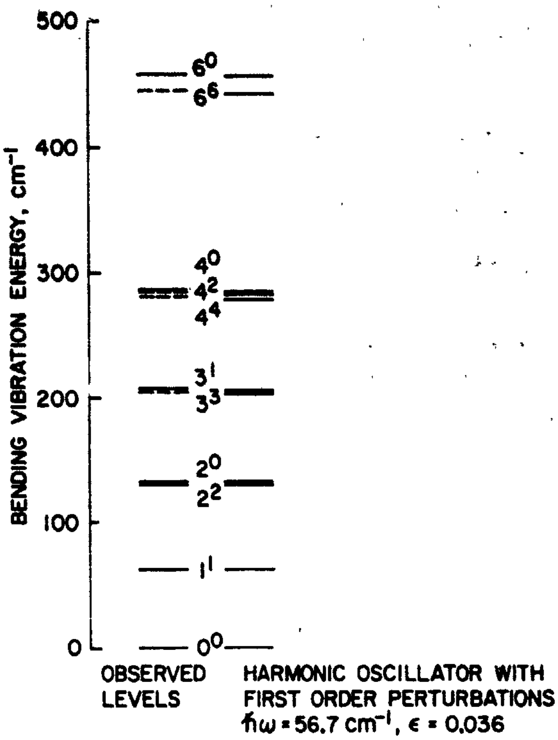

Figure 6.7.- Bending vibration energy levels observed for C_3 (--- levels unidentified but deduced from empirical fit to observed levels, ref. 4) and levels calculated from first-order perturbation of a harmonic oscillator model.

At the time this book was prepared, levels beyond v = 6 had not been identified for C_3. In any event, the above first-order perturbation model would not be suitable for extrapolation much beyond this level because the value of ε required to match the observed levels is large enough that second- and third-order perturbation terms will become important for the higher levels. The above results do serve, however, to show the magnitude of curvilinear motion effects and how these counterbalance the effects of a steeper than harmonic bending potential function to give the final pattern of energy levels observed.

The effect of curvilinear motion is the order of 5 percent on the average. This correction is large from the viewpoint of the spectroscopist, who attempts to closely fit observed energy levels with models, but the correction is a tractable one from the viewpoint of the thermodynamicist, who primarily wishes to deduce gas properties from the partition function. Note that the contribution of curvilinear motion is a relatively constant fraction of the total bending energy, independent of the quantum level involved. This means that effects of curvilinear motion can be approximately accounted for in a normal mode model merely by adjusting the potential function used. For example, a 5-percent smaller value of ω will approximate the average effects of curvilinear bending motion in C_3. In such cases, normal mode approximations can be extended beyond the usual small-amplitude limits where $\sin r/d \approx r/d$ and yet give reasonably good results. The bending of most other triatomic molecules is much less extreme than occurs in C_3; therefore, for these molecules, the effects of curvilinear motion are much smaller still and normal mode models are usually quite adequate.

An additional effect of large-amplitude bending in C_3 (not yet adequately analyzed at the time this book was written) is the l-doubling produced by vibration-rotation coupling. The centrifugal stretching forces and the Coriolis forces due to rotations about an axis perpendicular to the molecular axis both contribute to a perturbation that splits the usually degenerate bending levels in much the same manner as Fermi resonance. Nielsen (ref. 9) treated this problem thoroughly for harmonic bending vibrations, and the corrections are usually small until rather high rotational quantum numbers are considered. The effects are important in identifying exact energy levels by the spectroscopist but are usually second order so far as the partition function of linear triatomic molecules are concerned. C_3 is an exception. The Coriolis force coupling with bending modes is still small because the bending vibration velocities orthogonal to the rotation vector are so small, but the centrifugal stretch coupling with bending vibration is abnormally large because of the large amplitude or low frequency of bending. In addition, curvilinear motion effects are present. As a result, the bending mode energy levels are rapidly spread apart in proportion to $J(J + 1)$ as the total rotation quantum number J increases. The analysis of this effect can be carried forward by methods similar to those outlined above.

Problem 6.11: Consider the bending vibrations of a linear triatomic molecule with three equal mass atoms and a square-well, cylindrical potential function:

$$\begin{aligned} V(r) &= 0 , \quad r < a \\ &= \infty , \quad a < r \end{aligned}$$

where r is the displacement of the end atoms from the axis of symmetry. Assume that all other internal energy modes are decoupled. Set up the Schroedinger equation in cylindrical coordinates. What is the reduced mass in this equation?

Find the normalized wave-function solutions and the eigenvalues. Find a limiting expression for the eigenvalues at large quantum numbers. How do the eigenvalues vary with quantum number?

Problem 6.12: Consider a doubly degenerate vibrational mode with degeneracy $g_v = v + 1$ and a characteristic temperature Θ, but with the energy levels spaced as v^2:

$$E_v = v^2 k\Theta$$

Evaluate the partition function,

$$Q = \sum_{v=0}^{\infty} (v + 1)e^{-v^2\Theta/T}$$

for $T > \Theta$, approximating the summation with an integral and retaining terms of order $(T/\Theta)^{1/2}$.

What is the contribution to $E - E_0$, to C_v, and to S from these vibrational levels? For $T >> \Theta$, how does the limit compare with harmonic oscillator results?

6.12 VIBRATIONS OF n-ATOM POLYATOMIC MOLECULES

Molecules with more than three atoms have more intricate symmetry properties than the molecules considered so far, and the problem is then developed most systematically using group theory. However, the number of independent vibrational modes which exist for an arbitrary n-atom molecule can be deduced very simply. Of the $6n$ coordinates available to the molecule totally ($3n$ independent position and momentum coordinates each), six independent coordinates are dedicated to the center of mass, while four coordinates are associated with the rotational motions if the molecule is linear and six coordinates if the molecule is nonlinear. Thus, there exist $6n-10$ vibrational degrees of freedom for linear polyatomic molecules and $6n-12$ vibrational degrees of freedom for nonlinear polyatomic molecules. Two degrees of freedom are associated with each normal mode of vibration, so the total number of vibrational modes is $3n-5$ and $3n-6$ for linear and nonlinear n-atom molecules, respectively. Some of these may be degenerate because of molecular symmetry; the sum of the degeneracies for the vibrational modes must add up to the above number.

From the viewpoint of a thermodynamicist or aerodynamicist, the important task is to develop a reasonably accurate expression for the partition function of such n-atom molecules as may occur in various gasdynamic problems. The normal mode vibrational frequencies are available for most common molecules from spectroscopy; a few of these are listed for some triatomic molecules in table 6.2 and for some common four- and five-atom molecules in table 6.3. The degeneracy of each triatomic molecule vibration is unity, except for the linear molecules where the degeneracy of the bending vibration, ν_2, is two.

TABLE 6.2.- FUNDAMENTAL VIBRATIONS OF SOME TRIATOMIC MOLECULES

Molecule	Vibrational frequency, cm^{-1}			Bond angle, deg 2α
	ν_1	ν_2	ν_3	
O-C-O	1388*	667.3	2349	180
S-C-S	655	397	1510	180
H-C-N	2096	712	3312	180
O H H	3657	1595	3776	105
O D D	2666	1179	2789	105
H S S	2611	1183	2626	92
N-N-O	1285	589	2224	180
N O O	1306	755	1621	130
O O O	1110	705	1043	117
S O O	1151	518	1362	120

*Fermi resonance with 02^00, 1286 cm^{-1}.

TABLE 6.3.- FUNDAMENTAL VIBRATIONS OF SOME FOUR- AND FIVE-ATOM MOLECULES

Molecule	Vibrational frequency, cm^{-1}						Configuration
	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	
H-C-C-H	3373	1974	3282	613	731	----	Linear
H\ C-O H/	2780	1744	1503	2874	1280	1167	Planar
NH_3	3337	950	3444	1628	----	----	Pyramid
O\ S-O O/	1069	652	1330	532	----	----	Planar
CH_4	2916	1534	3019	1306	----	----	Tetrahedral
CH_3Cl	2966	1355	732	3043	1551	1017	Tetrahedral

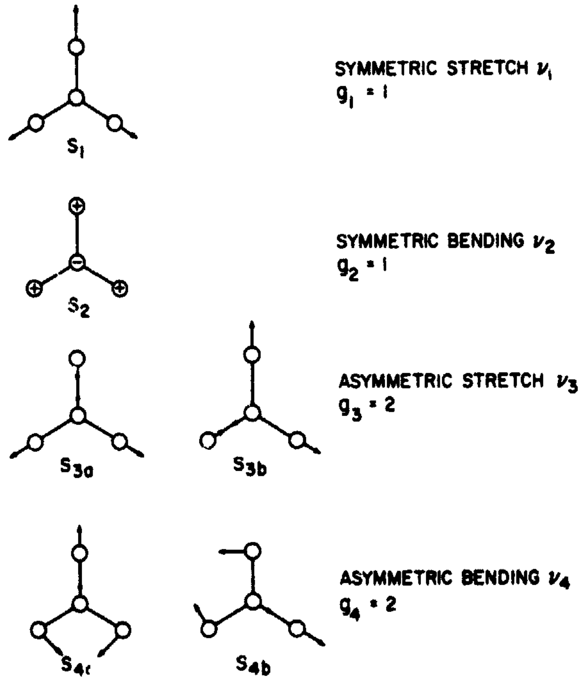

Figure 6.8.- Symmetry coordinates for the XY_3 molecule.

The degeneracies of the four- and five-atom molecules can often be deduced simply by considering possible symmetry coordinates, without resorting to group theory formalism. For example, figure 6.8 shows a set of symmetry coordinates for the XY_3 molecule. The symmetric stretch mode designated ν_1 has just one possible independent motion. The symmetric bending ν_2 that occurs out of the plane of the figure also has just one independent motion. However, the asymmetric stretch mode ν_3 has two different motions that give the same frequency. At first glance, one might surmise that three such vibrations are possible, corresponding to the approach of any one of the three equivalent Y atoms toward the center of mass as the other two Y atoms recede. The third motion depends on the other two, however, because of the requirement that the center of mass be fixed. For example, think of the central X atom as infinitely massive so that it stays at the center of mass. Then if the positions of two of the Y atoms are established, the third is automatically determined. Thus all possible positions of the outer atoms along the bond directions, for which the center of mass is constant, can be uniquely described by the two asymmetric stretch modes shown. The same situation exists for the asymmetric bending modes ν_4 for motions of the outer atoms at right angles to the bond directions. The degeneracy of this mode is again 2 since the position of any two of the outer atoms along these directions automatically fixes the position of the third, as for the infinite mass central atom case. In the actual molecule, the central atom has finite mass, of course, and it takes part in the normal coordinate motions, which are something like the symmetry coordinate motions shown. The infinite mass central atom case is merely helpful in separating the allowed degeneracies in a succinct way.

The XY_3 molecule may be planar as in SO_3, or pyramidal, with the equilibrium position of the central atom out of the plane of the three outer atoms, as in NH_3. In either case, the bending modes and their degeneracies are as shown in figure 6.8. If one of the outer atoms is substituted with a different atom, the degeneracies are removed and six different normal mode frequencies occur. Even the substitution of a different isotope splits the degenerate levels into closely spaced doublets. With highly sensitive spectrographs, weak isotope doublets are observed in such gases even under normal conditions because of traces of isotope species present in nature.

Figure 6.9 shows symmetry coordinates for vibrations of a linear symmetric X_2Y_2 molecule, such as acetylene. The stretch coordinates are chosen to isolate the vibrations of individual bonds; for most potential models, the normal stretch coordinates are simple linear combinations of these and will be along the axis of symmetry. The bending symmetry coordinates shown are the same as the bending normal coordinates for most potential models. In this case, the stretch modes ν_1, ν_2, and ν_3 clearly all have a degeneracy of 1, while the bending modes ν_4 and ν_5 have a degeneracy of 2, corresponding to the bending in the plane of the figure and out of the plane of the figure, just as for the linear triatomic molecule.

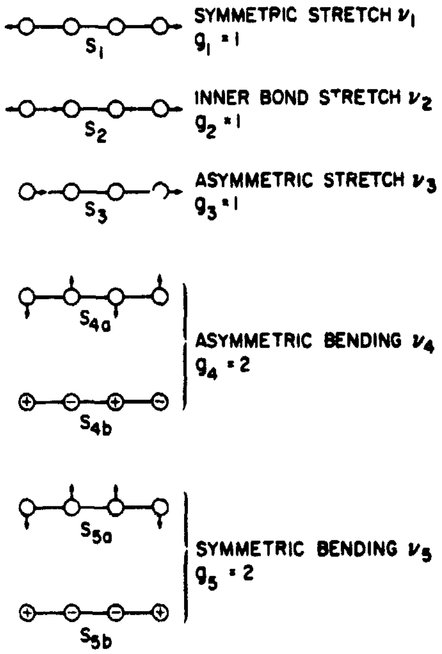

Figure 6.9.- Symmetry coordinates for the linear symmetric X_2Y_2 molecule.

Figure 6.10 shows symmetry coordinates for vibrations of a tetrahedral molecule with central atom XY_4, such as methane. In this case, the normal coordinates are complex combinations of the symmetry coordinates, or a similar such set, and lie along directions different from the bond directions, just as for the bent triatomic

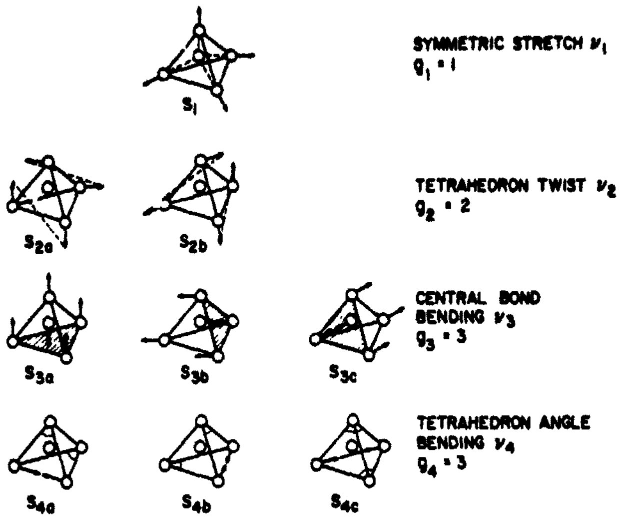

Figure 6.10.- Symmetry coordinates for the tetrahedral molecule with central atom, XY_4.

molecule. Again, it is helpful to consider the central atom as infinitely massive to separate the number of independent degenerate modes. The symmetric stretch mode ν_1 is again singly degenerate. The tetrahedron twisting mode ν_2 is doubly degenerate; a third set of opposing twistable edges are available in the tetrahedron, but again their positions are uniquely determined by the two twisting motions shown and the requirement that the center of mass be constant. The central bond bending motions are triply degenerate, corresponding to the motion of three of the tetrahedral faces toward and away from the central atom. Again, the motion of the fourth face of the tetrahedron is uniquely determined by the motion of the other three and the constant position of the center of mass. Finally, the tetrahedron angle bending is triply degenerate; three sets of two angles each partake in the vibrations shown, the fourth set again depends on the other three sets.

When one of the outer atoms is replaced by a different atom, as in methyl chloride CH_3Cl, some, but not all, of the degeneracies are removed. For example, in the central bond bending mode, the central atom moves toward a plane with two H atoms and one Cl atom in two possible ways, and toward a plane with three H atoms in one possible way. Thus the triply degenerate central bond bending mode is split into one doubly degenerate level and one singly degenerate level. Similarly, in the tetrahedron angle bending modes, the Cl atom sits at the vertex of one of the bending angles in one case, while an H atom sits at the vertex of both bending angles in the other two cases. Again, the triply degenerate level is split into one singly degenerate level and one doubly degenerate level. For the tetrahedron twisting modes, one of the twisted edges contains a Cl atom no matter which of the two opposing edges is chosen to describe the twisting motion, and this level remains doubly degenerate. Thus, one observes six independent vibrational frequencies for the CH_3Cl molecule (table 6.3). Assigning the allowed degeneracies to the observed frequencies is not always a simple matter, however, as this requires that a potential model be established which closely fits the observed frequencies.

In principle, one could continue to analyze yet more complex polyatomic molecules in this way. The reader can readily deduce the allowed degeneracies of CH_2Cl_2, for example, and can also appreciate that a tetrahedral molecule with two different substitutions, such as CH_2ClBr, will have a full set of nine singly degenerate energy levels. However, eventually, the pattern of symmetries becomes so complicated that some of the possible motions or their redundancies will likely be missed. The advantage of analyzing the proble with the formalism of group theory is to avoid such error. Nevertheless, the results are still based on the same type of physical and geometrical concepts introduced here in the discussion of the simpler polyatomic molecules.

6.13 CONCLUDING REMARKS

For the common, simple polyatomic molecules, the energy levels have been measured by spectroscopists, and the degeneracies have been assigned to these levels from an analysis of approximate potential models that fit the observed frequencies. In many cases, the harmonic oscillator model in normal mode coordinates adequately represents the data and, in this approximation, the contribution of molecular vibrations to the partition function and the derivative thermodynamic properties can all be expressed in closed analytic form. Effects of multiple degeneracy and of Fermi resonance between levels are treated by simple quantum theory with good quantitative accuracy. In principle, anharmonic corrections can be added in the same manner as for diatomic molecules, but the available experimental data do not always warrant such extensions of the analysis, particularly for molecules with more than three atoms. This occurs partly because complex polyatomic molecules all tend to break up and disappear from gases tested at temperatures high enough to excite upper vibrational levels of such molecules. The spectroscopist is unable to observe strong enough lines to identify and analyze in such cases. However, the thermodynamicist does not urgently need these data since these excited species do not normally appear in gases of interest with appreciable density. Thus, for many practical purposes, the limitations on derived thermodynamic properties set by lack of data is not serious.

In some cases, the anharmonic effects change all the eigenvalues by nearly a constant ratio (C_3 is an example). In such cases, the normal mode model can be extended beyond the range of small-amplitude vibrations merely by adjusting the frequency parameter to account for the deviations from normal harmonic oscillator behavior, at least to the accuracy required for partition function evaluation.

Polyatomic molecule structures can have a complicated symmetry, which determines the degeneracies of the vibrational modes involved. In extremely complex cases, the symmetry analysis is best performed by use of group theory. However, for many common molecular structures having up to five atoms, the symmetry properties can be deduced easily by inspection.

APPENDIX 6-A: HERMITIAN OPERATOR FOR $f(r)p^2$ IN CYLINDRICAL COORDINATES

Consider a term of the Hamiltonian expressed as the product of a general function of the radius r and the square of its conjugate momentum, in cylindrical coordinates,

$$H = f(r)p^2 \tag{6-A1}$$

where p is the radial momentum. The operator $\widetilde{H}$ for this function, which is used in the Schroedinger equation, is required to be Hermitian, that is, for any two eigenfunctions F and G of this equation, the operator in cylindrical coordinates must satisfy the relation (see appendix 3-A)

$$\int_0^\infty F(\widetilde{H}G)r\,dr = \int_0^\infty G(\widetilde{H}F)r\,dr \tag{6-A2}$$

For present purposes, the operator and the radial wave functions are all real, so we need not be concerned with the complex conjugate aspects of the Hermitian relations. The integrations over angle ϕ and axial coordinate z are presumed to be already performed in equation (6-A2). If p is simply replaced by a derivative of r in equation (6-A1), the resulting operator is not Hermitian because of the presence of radius r in the cylindrical coordinate volume element. However, equation (6-A1) may be expressed in equivalent form as

$$H = \frac{1}{2r}\left(f + r\frac{df}{dr}\right)p^2 r + \frac{1}{2}\left(f - r\frac{df}{dr}\right)p^2 \tag{6-A3}$$

Then, if momentum p is replaced by $i\hbar(\partial/\partial r)$, the resulting operator (used in eq. (6.98)) is Hermitian:

$$\widetilde{H} = -\hbar^2\left[f\frac{\partial^2}{\partial r^2} + \left(\frac{f}{r} + \frac{df}{dr}\right)\frac{\partial}{\partial r}\right] \tag{6-A4}$$

This may be verified by use of the operator in equation (6-A2):

$$\int_0^\infty F(\widetilde{H}G)r\,dr = -\hbar\left[\int_0^\infty F\frac{\partial^2 G}{\partial r^2}rf\,dr + \int_0^\infty F\frac{\partial G}{\partial r}\frac{d(rf)}{dr}\,dr\right] \tag{6-A5}$$

The second integral is readily integrated by parts, which gives a term that vanishes because of the boundary conditions on F and $\partial G/\partial r$, and a term that cancels the first integral, with the final result:

$$\int_0^\infty F(\widetilde{H}G)r\,dr = \hbar^2\int_0^\infty \frac{\partial F}{\partial r}\frac{\partial G}{\partial r}rf\,dr = \int_0^\infty G(\widetilde{H}F)r\,dr \tag{6-A6}$$

The special case $f = 1$ leads to the usual Laplacian operator for p^2 in cylindrical coordinates, of course.

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CHAPTER 7 - ELECTRONIC ENERGY STATES

7.1 SUMMARY

One-electron wave functions are reviewed and approximate solutions of two-electron systems are given in terms of these one-electron functions. The symmetry effects associated with electron spin are reviewed and the effects of electron exchange on energy levels of the two-electron system are given. The coupling of electronic orbital and spin angular momentum is considered next and the Landé interval rule for Russell-Saunders or LS coupling is derived. The configurations possible for various multi-electron LS couplings are enumerated (examples from the first two rows of the periodic table are given), and the meaning of the spectroscopic nomenclature is discussed, particularly with respect to the degeneracies of the electron states involved. Next the nomenclature, symmetries, and degeneracies for electron states of diatomic molecules are discussed, and some examples for N_2, O_2, and NO are presented. The electronic partition functions and derivative thermodynamic properties are expressed in terms of these energies and degeneracies, and examples are given for some of the simple gas species encountered in the earth's atmosphere.

7.2 INTRODUCTION

In addition to the rotational and vibrational energy states associated with the motion of atoms in molecules, the energy states associated with the motion of electrons about the atomic centers must be included in the total partition functions for both atoms and molecules. The electrons, conceived as classical particles, move in a potential field of combined Coulomb attractions and repulsions, they possess angular momentum, and they vibrate in the sense that their classical orbits periodically take them between minimum and maximum distances from the nuclear centers of charge, resulting in oscillating electric dipoles that can absorb and emit radiation. As expected then, the wave solutions, to the Schroedinger equation in polar coordinates involve spherical harmonics and Laguerre polynomials just as for rotational and vibrational motions of molecules. Unfortunately, the solutions for multi-electron atoms and for molecules cannot be obtained in simple analytic form. Relatively precise numerical computer solutions are feasible in many cases, but do not have great heuristic value. However, simple and exact analytic solutions are available for the one-electron atom, and the multi-electron atom and molecular electron wave functions can be approximated as linear combinations of products of one-electron atomic wave functions. Although this approximation does not lead to accurate quantitative results, it does permit one to classify the observed spectra and to assign quantum numbers, angular momentum values, and degeneracies to the observed energy levels. Spectroscopists have provided such precise values for the energy levels in many cases of interest that the difficulty of calculating these numbers is not a great handicap; with the degeneracies assigned, the thermodynamicist has all the necessary information to determine the partition functions and all the thermodynamic properties of gases that involve electronically excited atoms and molecules. Thus we start with a brief review of the wave function solutions for the one-electron atom (such as H, He^+, Li^{++}, etc.).

7.3 ONE-ELECTRON ATOMIC WAVE FUNCTIONS

Classically, the electron orbits the nuclear center of the atom under the influence of the Coulomb potential:

$$V = -\frac{Ze^2}{r} \tag{7.1}$$

where e is the charge on the electron, Ze is the charge on the nucleus, and r is the distance between them. The total energy of the motion is

$$E = \frac{p^2}{2\mu} - \frac{Ze^2}{r} \tag{7.2}$$

where μ is the reduced mass of the electron and the nuclear particle and p is the momentum. In this case, the nuclear mass m_n is so much larger than the electron mass m_e that the reduced mass is almost equal to the latter:

$$\frac{1}{\mu} = \frac{1}{m_n} + \frac{1}{m_e} \simeq \frac{1}{m_e} \tag{7.3}$$

According to the uncertainty principle, the electron cannot orbit infinitely close to the nucleus. The minimum value for momentum p_o corresponding to a minimum circular orbiting distance r_o is given by

$$p_o r_o = \hbar \tag{7.4}$$

and the ground state energy in equation (7.2) may accordingly be expressed as

$$E_o = \frac{\hbar^2}{2\mu r_o^2} - \frac{Ze^2}{r_o} \tag{7.5}$$

Since this must be the energy minimum,

$$\left(\frac{dE}{dr}\right)_{r_o} = -\frac{\hbar^2}{\mu r_o^3} + \frac{Ze^2}{r_o^2} = 0 \tag{7.6}$$

and the orbiting distance in the ground state is

$$r_o = \frac{\hbar^2}{Z\mu e^2} = \frac{\mu}{m_e}\frac{a}{Z} \simeq \frac{a}{Z} \tag{7.7}$$

where a is the Bohr radius $\hbar^2/m_e e^2$ (0.52917×10^{-8} cm), that is, the minimum orbit radius obtained where $Z = 1$ and the nuclear mass is infinite. From this point, the slight correction required for finite nuclear mass is neglected. The ground state energy given by equation (7.5) is

$$E_0 = -\frac{Z^2\mu e^4}{2\hbar^2} = -\frac{Z^2e^2}{2a} \tag{7.8}$$

The time-independent Schroedinger wave equation that rigorously describes the steady-state motion of an electron and a charged nucleus about their centers of mass is exactly the same as equation (5.1) used as the starting point for the analysis of diatomic molecule vibrations. With the potential in equation (7.1), this becomes

$$\nabla^2\psi + \frac{2\mu}{\hbar^2}\left(E + \frac{Ze^2}{r}\right)\psi = 0 \tag{7.9}$$

To simplify mathematical notation, the distance r is commonly expressed in units of a and the energies in units of e^2/a (27.21 eV). For the moment, we are concerned with negative values of energy between 0 and $-Z/2$, corresponding to bound states of the electron; positive energy states correspond to a free electron whose motion is merely deflected by the nuclear potential. Let the constant n be defined by

$$2E = -\frac{Z^2e^2}{n^2a} \tag{7.10}$$

In these units, equation (7.9) takes the form

$$\nabla^2\psi + \left(\frac{2Z}{r} - \frac{Z^2}{n^2}\right)\psi = 0 \tag{7.11}$$

Just as for the rotating, vibrating diatomic molecule, substitute the separable wave function $\psi(r,\theta,\phi) = Y(\theta,\phi)R(r)$ into equation (7.11), and obtain the result that Y is the usual spherical harmonic solution to the differential equation

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dY}{d\theta}\right) + \frac{1}{\sin^2\theta}\frac{d^2Y}{d\phi^2} + l(l+1)Y = 0 \tag{7.12}$$

where the angular momentum quantum number l must be an integer to obtain finite single valued functions, while R is the solution to

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \left[\frac{2Z}{r} - \frac{Z^2}{n^2} - \frac{l(l+1)}{r^2}\right]R = 0 \tag{7.13}$$

The last term in equation (7.13) corresponds to a potential from which the centrifugal force on the electron, because of its angular momentum, is derivable. Let ρ be a new dimensionless distance variable in units of a:

$$\rho = \frac{2Zr}{n} \tag{7.14}$$

In this variable, equation (7.13) takes the form

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left[\frac{n}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2}\right]R = 0 \tag{7.15}$$

Again factor out the asymptotic behavior at large ρ and a term ρ^l to allow for the singularity at the origin

$$R(\rho) = e^{-\rho/2}\rho^l L(\rho) \tag{7.16}$$

Substitute this into equation (7.15) to obtain

$$\rho\frac{d^2L}{\partial\rho^2} + [(2l+1) + 1 - \rho]\frac{dL}{d\rho} + [(n+l) - (2l+1)]L = 0 \tag{7.17}$$

which is the Laguerre equation (refs. 1 and 2). This equation has finite polynomial solutions provided n is a positive integer greater than $(l + 1)$. These polynomials are the same associated Laguerre functions introduced as solutions for the doubly degenerate bending modes of linear symmetric triatomic molecules in polar coordinates (eq. (6.83)), except that the indices on the Laguerre functions are related to the quantum numbers n and l differently:

$$L(\rho) = L_{n+l}^{2l+1}(\rho) \tag{7.18}$$

The total wave function for a single electron bound to a nucleus of charge Ze thus becomes

$$\psi(\theta,\phi,\rho) = Y_l^{\pm m}(\theta,\phi)N_{nl}\, e^{-\rho/2}\rho^l L_{n+l}^{2l+1}(\rho) \tag{7.19}$$

where Y_l^m is the normalized spherical harmonic function (eq. (4.34)) and N_{nl} is a constant normalizing to unity the integral of r^2RR^* over all values of r (see problem 7.1):

$$N_{nl} = \left\{\left(\frac{2Z}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right\}^{1/2} \tag{7.20}$$

Problem 7.1: Prove that the integral

$$\int_0^\infty R^2(r)r^2\,dr = \left(\frac{na}{2Z}\right)^3\int_0^\infty e^{-\rho}\rho^{2l+2}\left(L_{n+l}^{2l+1}\right)^2 d\rho = \left(\frac{1}{N_{nl}}\right)^2$$

as required to normalize the single-electron wave function. A procedure using the moment-generating functions can be followed as in problem (6.9) except the product $e^{-x}x^{s+1}U_sV_s$ should be integrated over all x from 0 to ∞ in this case:

$$\sum_{r,t=s}^{\infty} \frac{u^r v^t}{r!t!} \int_0^{\infty} e^{-x} x^{s+1} L_r^s L_t^s \, dx = \int_0 e^{-x} x^{s+1} U_s V_s \, dx = \frac{(uv)^s}{(1-u)^{s+1}(1-v)^{s+1}} \int_0^{\infty} x^{s+1} e^{-x(1-uv)/(1-u)(1-v)} \, dx$$

In expanding the results, isolate the terms where $r = t = n + l$ and $s = 2l + 1$.

The first few normalized radial wave functions are

$$R_{10} = (Z/a)^{3/2} 2 \, e^{-\rho/2}$$

$$R_{20} = \left(\frac{Z/a}{2}\right)^{3/2} (2 - \rho) e^{-\rho/2}$$

$$R_{21} = 3 \left(\frac{Z/a}{6}\right)^{3/2} \rho \, e^{-\rho/2}$$

$$R_{30} = \frac{1}{3} \left(\frac{Z/a}{3}\right)^{3/2} (6 - 6\rho + \rho^2) e^{-\rho/2}$$

$$R_{31} = \frac{2}{3} \left(\frac{Z/a}{6}\right)^{3/2} (4\rho - \rho^2) e^{-\rho/2}$$

$$R_{32} = \frac{10}{3} \left(\frac{Z/a}{30}\right)^{3/2} \rho^2 \, e^{-\rho/2}$$

Alternative sets of orthogonal wave functions may be formed from linear combinations of the above wave functions. For example, an alternative set often used to describe the three p orbitals ($n = 2$, $l = 1$) is

$$\psi_{px} = \frac{R_{21}(r)}{\sqrt{2}} [Y_1^{\,1}(\theta,\phi) + iY_1^{-1}(\theta,\phi)] = \sqrt{\frac{3}{4\pi}} \, R_{21}(r) \, \frac{x}{r}$$

$$\psi_{py} = -\frac{iR_{21}(r)}{\sqrt{2}} [Y_1^{\,1}(\theta,\phi) - iY_1^{-1}(\theta,\phi)] = \sqrt{\frac{3}{4\pi}} \, R_{21}(r) \, \frac{y}{r}$$

$$\psi_{pz} = R_{21}(r) Y_1^{\,0}(\theta,\phi) = \sqrt{\frac{3}{4\pi}} \, R_{21}(r) \, \frac{z}{r}$$

The best coordinate system depends on the symmetry of the problem to be solved. For example, where perturbations from an external field with a fixed direction arise, the wave functions are expressed most conveniently in parabolic coordinates (ref. 3).

The allowed energy levels are those given in equation (7.10) where n is required to be some integer from 1 to ∞; the energy is independent of the other quantum numbers l and m for the single electron. A degeneracy of states exists for which l takes n integer values from 0 to $(n - 1)$, and for each value of l there are $2l + 1$ states, corresponding to $\pm m$ taking values from $-l$ to l. Each state must be doubled to account for the spin degeneracy of the electron. Thus the total degeneracy of states is the sum of the arithmetic progression

$$g_n = 2 \sum_{l=0}^{n-1} (2l + 1) = 2[1 + 3 + 5 + 7 \; . \; . \; . \; (2n - 1)] = 2n^2 . \qquad (7.21)$$

In spectroscopic nomenclature, the states with zero angular momentum ($l = 0$) are called *s* states, the states with one unit of angular momentum ($l = 1$) are called *p* states, the $l = 2$ states are called *d* states, while the $l = 3$ states are called *f* states. This nomenclature was started long before quantum mechanics was developed and will undoubtedly persist. The nomenclature arose because of the appearance of the spectral lines observed due to optical transitions between various levels. The *s* states are responsible for a series of transitions that give very sharp lines, the *p* states produced very strong lines called the principal series, the *d* states produced a series of lines fuzzy or diffuse in appearance, and *f* stands for a series of lines known as the fundamental series. Higher angular momentum states are normally unobserved and therefore remained unnamed; these are now designated in alphabetical sequence: *g* for $l = 4$, *h* for $l = 5$, etc. Single-electron atomic term symbols are designated nl, where n is the total quantum number and the angular momentum is designated by the spectroscopists as *s*, *p*, *d*, *f*, etc. Thus a ground state electron is (1*s*), the first excited states are (2*s*) or (2*p*), the next level can be (3*s*), (3*p*), or (3*d*), and so forth.

The electrons in multi-electron systems have wave functions with properties similar to the one-electron wave functions and the total wave function can be approximated as a product of single-electron wave functions. Thus the ground state of two-electron systems such as He I, Li II, Be III, etc. (i.e., neutral He, Li^+, Be^{++}, etc.) is known as a $(1s)^2$ configuration, signifying two electrons in the ground state wave function with paired spin. According to the Pauli principle, no more electrons can occupy the (1*s*) state in the same physical space surrounding the nucleus, so subsequent electrons added to the system must occupy the two available (2*s*) states, then the six available (2*p*) states, then the two (3*s*) states, the six (3*p*) states, the ten (3*d*) states, and so on. Ground state configurations for the first few neutral atoms of the periodic table of elements are given, for example, in table 7.1. A similar sequency of electron configurations occurs for the singly ionized atoms He II, Li II, Be II, B II, etc., for the doubly ionized atoms Li III, Be III, B III, etc., and so on. A sequence such as He I, Li II, Be III, B IV, etc., is known as an isoelectronic sequence; the same number of electrons are involved and occupy similar states; only the energy levels are depressed as the nuclear charge grows larger.

For heavier atoms, the electrons perturb one another so that the lowest energy state does not sequentially follow the same order as the lowest energy configuration of one-electron states. The outer electrons with high angular momentum are more effectively screened from the nuclear charge by the inner electrons than are the outer electrons with low angular momentum. Thus, starting with potassium, the outer electron seeks the more tightly bound (lower energy) (4*s*) state in preference to the available (3*d*) states. The similar chemical and magnetic properties of ferrous metal and rare earth

TABLE 7.1.- ELECTRON CONFIGURATIONS FOR GROUND STATE ATOMS

Nuclear charge Z	Atom	Electron configuration shell		
		K	L	M
1	H	$(1s)$		
2	He	$(1s)^2$		
3	Li	$(1s)^2$	$(2s)$	
4	Be	$(1s)^2$	$(2s)^2$	
5	B	$(1s)^2$	$(2s)^2(2p)$	
6	C	$(1s)^2$	$(2s)^2(2p)^2$	
7	N	$(1s)^2$	$(2s)^2(2p)^3$	
8	O	$(1s)^2$	$(2s)^2(2p)^4$	
9	F	$(1s)^2$	$(2s)^2(2p)^5$	
10	Ne	$(1s)^2$	$(2s)^2(2p)^6$	
11	Na	$(1s)^2$	$(2s)^2(2p)^6$	$(3s)$
.	.	.	.	.
.	.	.	.	.
.	.	.	.	.

sequences of elements are related to the exsitence of similar configurations of s and p electrons in the high quantum number shells, while lower quantum number orbits with higher angular momentum remain incompletely filled.

To see how these one-electron wave functions are useful in approximating multi-electron wave functions and classifying their energy states, consider two-electron atoms (such as He I, Li II, Be III, etc.) as the simplest example of bound state multi-electron systems. First, consider total wave functions that are simple products of two one-electron wave functions; then consider linear sums of such product wave functions that satisfy the Pauli asymmetry principle, which improve the simple product wave functions, as a basis for classifying and modeling multi-electron systems.

7.4 TWO-ELECTRON ATOMIC WAVE FUNCTIONS

The Hamiltonian operator for two electrons moving in the field of nuclear charge Z, where distance is given in units of a (eq. (7.7)) and the potential in units of e^2/a is, neglecting the effects of electron spin,

$$H = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_2} + \frac{1}{r_{12}} \tag{7.22}$$

where r_1 and r_2 are the distances between the nucleus and each electron and r_{12} is the distance between the two electrons, $|\vec{r}_1 - \vec{r}_2|$. The term ∇_i^2 is the Laplacian operator in the variables r_i, θ_i, and ϕ_i; to the approximation nuclear mass is considered infinite, $-(1/2)\nabla_i^2$ represents the kinetic energy of the ith electron.

The average effect of each electron is to partially screen the central charge from the other electron and, to a first approximation, this situation is expected to be modeled by

$$H = -\left(\frac{1}{2}\nabla_1{}^2 + \frac{b_1}{r_1}\right) - \left(\frac{1}{2}\nabla_2{}^2 + \frac{b_2}{r_2}\right) \tag{7.23}$$

where b_1 and b_2 are the effective screened nuclear charges seen by electron 1 and 2, respectively, both somewhat smaller than the actual nuclear charge Z. When the Hamiltonian can be separated into a sum of uncoupled terms in this manner, a solution to the Schroedinger equation is the product of solutions to each term of the sum (see problem 6.1 where the Hamiltonian for vibrating polyatomic molecules is assumed to be separable into normal coordinates):

$$\psi = u(r_1,\theta_1,\phi_1)v(r_2,\theta_2,\phi_2) \tag{7.24}$$

For the ground state of He-like atoms (He I, Li II, Be III, etc.), both electrons occupy the same quantum cell of physical space and we assume that each electron "sees" the same screened potential ($b_1 = b_2 = b$). The wave function solution to the Schroedinger equation with the approximate Hamiltonian of equation (7.23) is then

$$\psi = \frac{b^3}{\pi} e^{-b(r_1+r_2)} \tag{7.25}$$

The two terms of the approximate Hamiltonian operating on this wave function each yield

$$-\left(\frac{1}{2}\nabla_i{}^2 + \frac{b}{r_i}\right)\psi = -\frac{b^2\psi}{2} = E_i\psi \tag{7.26}$$

and the total energy for the ground state predicted by this model is the sum $E_1 + E_2 = -b^2$, in units of e^2/a.

Problem 7.2: Prove that the Hamiltonian in equation (7.23) operating on the wave function in equation (7.25) in the Schroedinger equation $H\psi = E\psi$ yields the total energy $-b^2$.

The difference between the ground state energy of the helium-like atom and the ground state energy of the single-electron system for the same nuclear charge Z is an experimentally known quantity, which we use to determine the screened charge b. The ground state energy after one-electron detachment (where the wave function takes the form $C\,e^{-Zr}$) is rigorously given by

$$E = \frac{H\psi}{\psi} = -\frac{\left(\frac{1}{2}\nabla^2 + \frac{Z}{r}\right)C\,e^{-Zr}}{C\,e^{-Zr}} = -\frac{Z^2}{2} \tag{7.27}$$

Thus the one-electron detachment energy I is

$$I = b^2 - \frac{Z^2}{2} \tag{7.28}$$

For He I, $Z = 2$ and I is just the energy of single-electron ionization to He II, known to be 24.58 eV or 0.903 units of e^2/a.[1] Thus the value of b which fits this model to observed He energy levels is

$$b = \sqrt{I + \frac{Z^2}{2}} = 1.704 \tag{7.29}$$

The average energy of a given trial wave function ψ obtained with the exact Hamiltonian (in this case, eq. (7.22)) is the integral

$$\bar{E} = \int \psi^* H \psi \, d\tau \tag{7.30}$$

According to the variational method (refs. 2 and 4), the best trial wave function of a given form is the one that minimizes $\bar{E}$. In the present case, the variational method gives $Z_1 = 1.688$, not very different from that given above for the simple screened charge model of the Hamiltonian. Of course, a small difference in the exponent b makes a large percentage difference in the wave function at large r. In those regions, the variational wave function would be closer to reality than the screened charge type of wave function. Considerably better agreement with observed energy levels can be obtained by adding some additional terms to the trial wave function used in the variational method. However, the involved mathematical exercise required to calculate these variational wave functions does not teach us much additional physics, and the method is not very suitable for developing approximate excited state wave functions. (The variational method can be used for excited states by imposing the requirement that the trial wave function be orthogonal to the trial wave functions for all lower-level states and minimizing the average energy. However, the errors are cumulative in this case and the excited state wave functions become rather poor approximations, even when very complex functions are used.) To understand and classify excited-state, two-electron systems, we return to solutions of the approximate Hamiltonian given in equation (7.23).

Usually, the only excited states deduced from observed transitions are those where one electron remains in the ground state configuration (1*s*) while the other is promoted to an excited state configuration (*nl*). In this case, a reasonably good approximation is to assume that the inner, or ground state, electron sees the full nuclear charge Z, while the outer, or excited, electron sees the screened charge b which is less than Z, and can be fit to the actual energy level by use of the approximate Hamiltonian. We can anticipate that the inner electron will neutralize almost one full charge of the nucleus in the outer regions where the excited electron probability is high, and that

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[1] The nomenclature He I, He II, He III is a spectroscopic notation merely signifying the neutral state, the singly ionized state, and the doubly ionized state of helium. This notation has no connection with the He I and He II notations used to signify different phases of liquid helium near the critical temperature in section 3.7. In atoms with more electrons, the notation continues with IV, V, etc., representing the triply ionized state, quadruply ionized state, etc. of the atom, respectively.

b will be very nearly $Z - 1$. The product wave function for the excited state configuration (1s) (nl) is taken to be

$$\psi_{nl} = \frac{Z^{3/2}\, e^{-Zr_1}}{\pi^{1/2}} R_{nl}\left(\frac{2br_2}{n}\right) Y_l(\theta_2,\phi_2) \tag{7.31}$$

The separable Hamiltonian to be used with this wave function is

$$H = -\left(\frac{1}{2}\nabla_1{}^2 + \frac{Z}{r_1}\right) - \left(\frac{1}{2}\nabla_2{}^2 + \frac{b}{r_2}\right) \tag{7.32}$$

The energy obtained with this Hamiltonian is

$$E_{nl} = \frac{H\psi}{\psi} = -\frac{Z^2}{2} - \frac{b^2}{2n^2} \tag{7.33}$$

and the constant b can be fit to the observed energy levels. For example, the first excited state configuration (1s) (2s) for He I is observed to occur at $E = -2.124\ e^2/a$, and a value of $b = 0.996$ fits equation (7.33) to this level. For higher excited states, b is found to be unity, suggesting that for these states the outer electron is well approximated by a purely hydrogen-like wave function and the interaction term r_{12}^{-1} in the exact Hamiltonian (eq. (7.22)) can be accounted for quite well by the screened charge approximation. This model can be extended to more electrons, and Slater and Frank (ref. 5) have suggested some empirical values for the screening parameters for various hydrogen-like wave functions which can be used to build up simple-product-type wave functions for the multi-electron case. However, these wave functions are not very exact, and even for purposes of classifying energy states, they lack an essential property - namely, the asymmetry property required by the Pauli principle. Therefore, we construct linear combinations of product-type wave functions that have the required symmetry to understand the role the Pauli principle plays in classifying states. The wave functions obtained are considerably better than the simple one-term products. However, the best wave functions are obtained by the numerical Hartree-Fock method (ref. 6) or refinements of that method (ref. 7).

Again consider the two-electron case as the example for the multi-electron system in general. Let u and v represent the spatially dependent part of the one-electron wave functions used to construct the total wave function and α and β, the electron spin functions. A linear combination of matrix elements satisfying the Pauli principle that the total wave function be asymmetric is

$$\psi = \begin{vmatrix} u(1)\alpha(1) & v(1)\beta(1) \\ u(2)\alpha(2) & v(2)\beta(2) \end{vmatrix} \pm \begin{vmatrix} u(1)\beta(1) & v(1)\alpha(1) \\ u(2)\beta(2) & v(2)\alpha(2) \end{vmatrix} \tag{7.34}$$

where the index i in $u(i)$ or $v(i)$ indicates that these one-electron factors are functions of the coordinates of the ith electron. The wave function obtained when the matrices are added is designated ψ_s:

$$\psi_s = [u(1)v(2) + u(2)v(1)][\alpha(1)\beta(2) - \alpha(2)\beta(1)] \tag{7.34a}$$

where subscript s denotes that the spatially dependent part of the wave function is symmetric. The two-electron spin function is then asymmetric in accord with the Pauli principle. The function obtained when the matrices are subtracted is designated ψ_a:

$$\psi_a = [u(1)v(2) - u(2)v(1)][\alpha(1)\beta(2) + \alpha(2)\beta(1)] \tag{7.34b}$$

where subscript a denotes asymmetry of the spatially dependent part of the wave function. The two-electron spin function is symmetric in this case.

The asymmetric function ψ_a vanishes if $u = v$; however, if $u \neq v$, the one-electron spin states could both be α or both be β. Thus two additional asymmetric states are permitted by the Pauli principle:

$$\left.\begin{aligned} \psi_a &= [u(1)v(2) - u(2)v(1)]\alpha(1)\alpha(2) \\ \psi_a &= [u(1)v(2) - u(2)v(1)]\beta(1)\beta(2) \end{aligned}\right\} \tag{7.34c}$$

The symmetric state ψ_s cannot exist with electrons in the same spin state, as the wave function vanishes in this case (let $\alpha = \beta$ in eq. (7.34a)). Thus the asymmetric states form a triplet set, while the symmetric state is a singlet. The symmetry properties that should be assigned to wave functions associated with observed levels of He I, for example, are immediately apparent from the singlet and triplet grouping of these levels.

The mathematical character of the Pauli symmetrized wave functions suggests that each electron is partly in wave function u and partly in wave function v. This characteristic is known as electron exchange. The effect of exchange is to split the singlet energy levels from the triplet levels.

7.5 ENERGY LEVELS OF TWO-ELECTRON SYSTEMS WITH EXCHANGE

In the last section, linear combinations of one-electron wave functions were found to satisfy the observed symmetry properties of multi-electron systems. Now, we derive expressions for the energy of these approximate, symmetrized wave functions for the two-electron system. The effect of spin momentum on energy is neglected for the moment so the Hamiltonian can be expressed as a function of the spatial coordinates of electrons 1 and 2 only. Let

$$H = H_1 + H_2 + H' = -\left(\frac{\nabla_1^2}{2} + \frac{Z}{r_1}\right) - \left(\frac{\nabla_2^2}{2} + \frac{Z}{r_2}\right) + H'(r_1, r_2) \tag{7.35}$$

where Z represents an average screened charge seen by both electrons, and the perturbation H' is a symmetrical function of r_1 and r_2, such as r_{12}^{-1}, added to account for coupling between the electrons. The trial wave function to be used in the Schroedinger equation is

$$\psi = u(1)v(2) \pm v(1)u(2) \tag{7.36}$$

where the plus sign is associated with the singlet function ψ_s and the negative sign with the triplet function ψ_a (as discussed in section 7.4). The appropriate two-electron spin function is a multiplicative factor, but since spin coordinates do not enter the approximate Hamiltonian used, the spin functions do not influence the calculation of energy and are omitted for mathematical convenience. The functions u and v are now taken to be normalized one-electron functions for unperturbed states about the central charge Z:

$$-\left(\frac{\nabla^2}{2} + \frac{Z}{r}\right) u = E_u u \tag{7.37a}$$

$$-\left(\frac{\nabla^2}{2} + \frac{Z}{r}\right) v = E_v v \tag{7.37b}$$

Normalizing the total wave function requires multiplication by the reciprocal of the integral

$$\begin{aligned}\int\psi^2\, d\tau_1\, d\tau_2 &= \int u_1{}^2\, d\tau_1 \int v_2{}^2\, d\tau_2 \pm 2\int u_1 v_1\, d\tau_1 \int u_2 v_2\, d\tau_2 + \int v_1{}^2\, d\tau_1 \int u_2{}^2\, d\tau_2\\ &= 2(1 \pm S^2)\end{aligned} \tag{7.38}$$

where S is the overlap integral

$$S = \int uvr^2 \sin\theta\, d\theta\, d\phi\, dr \tag{7.39}$$

which, in the present case, is either 1 or 0, depending on whether u and v are the same function or not. In problem 7.3, we consider one-electron wave functions for electrons moving in the fields of different effective nuclear charges. Then u and v are not orthogonal in general, and the overlap integral may be finite even where u and v are different.

Substitute the wave function of equation (7.36) and the Hamiltonian of equation (7.35) into the Schroedinger equation to obtain

$$\begin{aligned}E\psi &= H_1 u_1 v_2 + u_1 H_2 v_2 + H' u_1 v_2 \pm (H_1 v_1 u_2 + v_1 H_2 u_2 + H' v_1 u_2)\\ &= (E_u + E_v) u_1 v_2 + H' u_1 v_2 \pm [(E_u + E_v) v_1 u_2 + H' v_1 u_2]\end{aligned} \tag{7.40}$$

The value of E given in equation (7.40) is not a constant as it should be if ψ were an exact solution to the Schroedinger equation. However, the average value of E is a constant that is taken to be an approximation to the true eigenvalue. Multiply equation (7.40) by ψ:

$$\psi E \psi = (E_u + E_v)(u_1{}^2 v_2{}^2 + v_1{}^2 u_2{}^2) + (H' u_1{}^2 v_2{}^2 + H' v_1{}^2 u_2{}^2)$$

$$\pm 2[(E_u + E_v) u_1 v_1 u_2 v_2 + H' u_1 v_1 u_2 v_2] \tag{7.41}$$

Integrate equation (7.41) over all space to obtain

$$\overline{E} = (E_u + E_v) + \frac{K}{1 \pm S^2} \pm \frac{J}{1 \pm S^2} \tag{7.42}$$

where K and J are the Coulomb and exchange integrals

$$K = \int H' u_1{}^2 v_2{}^2 \, d\tau_1 \, d\tau_2 = \int H' v_1{}^2 u_2{}^2 \, d\tau_1 \, d\tau_2 \tag{7.43}$$

$$J = \int H' u_1 v_1 u_2 v_2 \, d\tau_1 \, d\tau_2 \tag{7.44}$$

The Coulomb integral derives its name because, when $H' = |\vec{r}_2 - \vec{r}_1|^{-1}$, the integral represents the average Coulomb repulsion between a charge distribution u^2 and a charge distribution v^2. However, the name is retained for arbitrary functions H', and the two integrals that define K in equation (7.43) are equal provided H' is symmetrical in r_1 and r_2. The exchange integral derives its name because the splitting of energy levels between symmetric and asymmetric states that results when electron exchange effects are included in the wave function is given by this integral. For the ground state, u and v are the same function and only the singlet state is allowed:

$$\overline{E_s} = 2E_u + \frac{K}{2} + \frac{J}{2} \tag{7.42a}$$

For excited states, u and v are different functions and

$$\overline{E_s} = E_u + E_v + K + J \tag{7.42b}$$

$$\overline{E_a} = E_u + E_v + K - J \tag{7.42c}$$

The exchange integral can be approximately evaluated as half the difference between observed singlet and triplet state energies:

$$J \simeq \frac{1}{2} (E_s - E_a) \tag{7.45}$$

while the Coulomb integral can be estimated from the difference between the observed energies and the calculated one-electron energies as

$$K \simeq \frac{1}{2} (E_s + E_a) - (E_u + E_v) \tag{7.46}$$

A somewhat better approximation for the wave function is obtained when u and v are taken to be one-electron wave functions for electrons moving in the field of different effective nuclear charges. The results of this approximation are sketched in problem 7.3, and the details of the derivation, following the above pattern, are left to the reader.

Problem 7.3: Again let the Hamiltonian be given by equation (7.35) and assume a wave function of the form of equation (7.36). Now, however, let u and v be single-electron wave functions for electrons moving in the field of central charges a and b, respectively:

$$-\frac{\nabla^2}{2}u = \left(-\frac{a^2}{2n_a{}^2} + \frac{a}{r}\right)u = \left(E_u + \frac{a}{r}\right)u \tag{7.37c}$$

$$-\frac{\nabla^2}{2}v = \left(-\frac{b^2}{2n_b{}^2} + \frac{b}{r}\right)v = \left(E_v + \frac{b}{r}\right)v \tag{7.37d}$$

where n_a and n_b are integer quantum numbers associated with the wave functions u and v, respectively. Generally, a and b are different and the overlap integral S (eq. (7.39)) is finite unless the spherical harmonic parts of the wave functions are orthogonal. However, the wave functions for different states maximize at different radial distances and oscillate in sign at different positions, so the overlap integral can be anticipated to be sizably less than unity and to grow smaller as the difference between quantum numbers increases, that is, as one of the electrons becomes more highly excited.

Show that the average energy obtained from the Schroedinger equation is now

$$\overline{E} = (E_u + E_v) + \frac{K + (a - Z)\left\langle\frac{1}{r}\right\rangle_{uu} + (b - Z)\left\langle\frac{1}{r}\right\rangle_{vv}}{1 \pm S^2} \pm \frac{J + (a + b - 2Z)S\left\langle\frac{1}{r}\right\rangle_{uv}}{1 \pm S^2} \tag{7.42d}$$

where the averages $\langle 1/r\rangle_{uu}$, $\langle 1/r\rangle_{vv}$, and $\langle 1/r\rangle_{uv}$ are given by

$$\left\langle\frac{1}{r}\right\rangle_{uu} = \int \frac{u^2}{r}\,d\tau$$

$$\left\langle\frac{1}{r}\right\rangle_{vv} = \int \frac{v^2}{r}\,d\tau$$

$$\left\langle\frac{1}{r}\right\rangle_{uv} = \int \frac{uv}{r}\,d\tau$$

and K and J are given by equations (7.43) and (7.44) as before. Note that if

$$K' = K + (a - Z)\left\langle\frac{1}{r}\right\rangle_{uu} + (b - Z)\left\langle\frac{1}{r}\right\rangle_{vv}$$

and

$$J' = J + (a + b - 2Z)S\left\langle\frac{1}{r}\right\rangle_{uv}$$

the result reduces to the same form as equation (7.42). According to the variational principle (refs. 2 and 4), the average energy given by the approximate wave functions used with the exact Hamiltonian in the Schroedinger equation is always greater than the true eigenvalue. With a and b both adjustable, the energy of the ground state can be minimized below the minimum value obtained when these are equal, and a somewhat better wave function is thus obtained. For highly excited states, one expects $a \approx Z$ and $b \approx Z - 1$ to be reasonable first approximations. In this case, $K' \approx K - \langle 1/r\rangle_{vv}$ and $J' \approx J - \langle 1/r\rangle_{uv}S$.

To this point, coupling between electron spin and orbital angular momentum has been ignored. This coupling produces small, additional shifts in energy level, with the result that triplet states appear as a trio of closely spaced states rather than a single energy level of degeneracy three.

7.6 EFFECTS OF COUPLED ELECTRONIC ANGULAR MOMENTUM

A charged particle with angular momentum, either as a result of spin or orbital motion, is observed to have a dipole moment with an associated magnetic field. The dipole moment of an electron interacts with the magnetic dipoles of the other electrons and with the magnetic field produced by the relative motion of the nuclear charge. The dipole moment μ associated with the orbital angular momentum p is observed to be

$$\vec{\mu} = \left(\frac{e}{2m_e c}\right)\vec{p} \tag{7.47}$$

The constant ratio between dipole moment and angular momentum, $e/2m_e c$, is known as the gyromagnetic ratio.

Problem 7.4: The dipole moment generated by a current i circulating in a single plane is defined as

$$\mu = \frac{iA}{c}$$

where A is the area swept out by the current loop. Show that for a charge e moving at constant velocity and in a circle of radius a, the dipole moment is given by equation (7.47). This same relation holds for any orbit with constant angular momentum, that is, for the motion of an electron in a central field.

Spin angular momentum also produces a magnetic dipole but in this case quantum effects lead to a gyromagnetic ratio twice as large as for the orbital angular momentum:

$$\vec{\mu}_s = \left(\frac{e}{m_e c}\right)\vec{s} \tag{7.48}$$

Problem 7.5: Assume a hypothetical classical particle with an arbitrary spherical mass distribution and arbitrary spherical charge distribution. Show that the gyromagnetic ratio for this particle spinning with a circular frequency ω is

$$\frac{\mu}{p} = \frac{e}{2mc}\,\frac{\langle r^4\rangle_e/\langle r^2\rangle_e}{\langle r^4\rangle_m/\langle r^2\rangle_m}$$

where $\langle r^n\rangle_m$ and $\langle r^n\rangle_e$ signify the nth moment of r with respect to the mass distribution and the charge distribution functions, respectively. Show that if charge is uniformly distributed over the surface at the radius r_o, and mass is distributed inversely proportional to the radius out to r_o, the observed gyromagnetic ratio is satisfied. Show that a similar result can be obtained from cylindrical charge and mass distributions if the charge is uniformly distributed over the edge of a disk and the mass is uniformly distributed throughout the disk. These distributions have no particular physical significance; they merely illustrate types of hypothetical classical particles having the observed gyromagnetic ratio for spin momentum.

The coupling of angular momentum can be illustrated by a semiclassical model for coupled spin and orbital momentum in a single-electron atom. The electron moving in an electric field $\vec{E}$ with velocity $\vec{v}$ experiences a magnetic field $\vec{H}$:

$$\vec{H} = \frac{\vec{E} \times \vec{v}}{c} \tag{7.49}$$

Since the field results from a spherically symmetric potential $V(r)$,

$$\vec{E} = (grad\ V)\,\frac{\vec{r}}{r} \tag{7.50}$$

The magnetic field becomes,

$$\vec{H} = \frac{grad\ V}{cr}\,\vec{r} \times \vec{v} \tag{7.51}$$

The cross product $\vec{r} \times \vec{v}$ is just the angular momentum divided by the mass, which remains constant in the central field:

$$\vec{H} = \frac{grad\ V}{mcr} \vec{p} \tag{7.51a}$$

The potential energy of coupling between the spin magnetic moment $\vec{\mu}_s$ and the magnetic field is

$$\Delta E = \langle \vec{\mu}_s \cdot \vec{H} \rangle = \frac{e}{m^2c^2} \left\langle \frac{grad\ V}{r} \right\rangle \vec{s} \cdot \vec{p} \tag{7.52}$$

where $\langle (grad\ V)/r \rangle$ is the averaged value:

$$\left\langle \frac{grad\ V}{r} \right\rangle = \int \psi^* \left(\frac{grad\ V}{r} \right) \psi\ d\tau \tag{7.53}$$

Quantum mechanically, $\vec{p}$ and $\vec{s}$ are limited to the values

$$\vec{p} = \hbar \vec{l}^* \tag{7.54}$$

$$\vec{s} = \hbar \vec{s}^* \tag{7.55}$$

where $\vec{l}^*$ and $\vec{s}^*$ are vectors with the magnitudes $\sqrt{l(l+1)}$ and $\sqrt{s(s+1)}$, respectively, and l is any integer while $s = 1/2$. The vector product is also limited to quantized values with total angular momentum $\hbar \vec{j}^*$, where $\vec{j}^*$ is a vector of magnitude $\sqrt{j(j+1)}$ and j takes the values from $|l + s|$ to $|l - s|$ in integer steps:

$$j^{*2} = l^{*2} + 2\vec{s}^* \cdot \vec{l}^* + s^{*2} = j(j+1) \tag{7.56}$$

Substituting the value of $\vec{s}^* \cdot \vec{l}^*$ from equation (7.56), one obtains for ΔE:

$$\Delta E = \frac{e\hbar^2}{2m^2c^2} \left\langle \frac{grad\ V}{r} \right\rangle [j(j+1) - l(l+1) - s(s+1)] \tag{7.57}$$

The measured value of ΔE, for a given l and s and various allowed values of j, in effect provides a measure of the average $\langle (grad\ V)/r \rangle$. This may be either positive or negative, depending on the wave functions involved. For a single electron moving in the field of a fixed central charge Ze, this becomes

$$\left\langle \frac{grad\ V}{r} \right\rangle = Ze \left\langle \frac{1}{r^3} \right\rangle \tag{7.58}$$

If r is expressed in units of the Bohr radius a and energy in units of two Rydbergs, e^2/a:

$$\frac{\Delta E}{e^2/a} = \frac{Z\alpha^2}{2} \left\langle \left(\frac{a}{r} \right)^3 \right\rangle [j(j+1) - l(l+1) - s(s+1)] \tag{7.59}$$

where α is the fine structure constant $e^2/\hbar c$ or $e\hbar/mca$, with the value 7.283×10^{-3}.

Problem 7.6: Pauling and Wilson (ref. 2) give the result for hydrogen-like wave functions

$$\left\langle\left(\frac{a}{r}\right)^3\right\rangle_{n,l} = \frac{Z^3}{n^3 l\left(l + \frac{1}{2}\right)(l + 1)}$$

The energy levels for these wave functions relative to the ground state level, neglecting l,s coupling, is

$$E_{n,l} = Z^2 R\left(1 - \frac{1}{n^2}\right)$$

where R is the Rydberg constant. Use $R = 109{,}679\ \text{cm}^{-1}$ for hydrogen and calculate the energy levels with l,s coupling for the $2s(j = 1/2)$, $2p(j = 1/2)$, and $2p(j = 3/2)$ levels. Compare with the observed levels.

Observed Hydrogen Energy Levels

Configuration	J	Energy above ground state, cm^{-1}
$1s$	1/2	0
$2p$	1/2	82258.907
$2s$	1/2	82258.942
$2p$	3/2	82259.272

The l,s coupling is seen to be very small in hydrogen. However, it increases with nuclear charge as Z^4 and becomes more pronounced in heavier atoms.

In multi-electron atoms and molecules, the magnetic dipoles due to spin and orbital electron motion all interact with one another as well as with the magnetic field due to the nuclear charge. For example, the dipole moment of electron i has a magnetic field at the location of electron j, with the components

$$H_r = \frac{2\mu}{r_{ij}^3} \cos \theta_{ij} \tag{7.60a}$$

$$H_\theta = \frac{\mu}{r_{ij}^3} \sin \theta_{ij} \tag{7.60b}$$

where r_{ij} is the distance between the electrons and θ_{ij} is the angle between the dipole moment $\vec{\mu}_i$ and the radius vector $\vec{r}_{ij}$.

The potential energy of coupling between a given dipole moment μ_i and the magnetic fields of the other dipoles is

$$\Delta E = \left\langle \vec{\mu}_i \cdot \sum_i \vec{H}_i \right\rangle \tag{7.61}$$

The averages are more difficult to evaluate in this case than in equation (7.52), which involved the coupling of a single electron's spin with its own orbital motion. From equation (7.60), the averages for multi-electron atoms are seen to involve averages such as r_{ij}^{-3} and averages over functions of the angles θ_{ij}, which take quantized values in accord with equations such as (7.56).

Some useful qualitative ideas about the grouping of energy levels in multi-electron systems can be gained by considering a model in which strongly interacting dipoles are coupled to give a relatively constant resultant angular momentum. Then weaker interactions are accounted for by coupling these resultant vectors so that they precess slowly about a total angular momentum vector. For example, in light atoms the coupling between the spin of an electron and its own orbital motion was seen to be very weak (see problem 7.6). The averages involved in equation (7.61) give much stronger coupling between the orbital motion and the orbital motion of the other electrons, also between the spin and the spin dipoles of the other electrons. Consequently, as a first approximation, the orbital momentum vectors are assumed to couple, as they would in the absence of spin perturbations, to give a resultant orbital angular momentum vector $\vec{L}^*$ with the magnitude $\sqrt{L(L+1)}$, where L is a constant, integer, total orbital momentum quantum number, which may be expressed as the sum

$$L = \sum_i l_i \cos \gamma_i \tag{7.62}$$

where l_i is the integer quantum number of orbital momentum for electron i, and the projections $l_i \cos \gamma_i$ are allowed to take all integer values between $+l_i$ and $-l_i$, in accord with the usual quantum selection rules in the absence of spin perturbations.

Similarly, the spin vectors are coupled to give a total resultant spin vector $\vec{S}^*$ of magnitude $\sqrt{S(S+1)}$, with a constant spin quantum number S that may be expressed as

$$S = \sum_i s_i \tag{7.63}$$

In this case, the projections s_i can take only the values ±1/2 and the sum is an algebraic sum.

Finally, the vectors $\vec{L}^*$ and $\vec{S}^*$ are coupled to give a total angular momentum vector $\vec{J}^*$ with the magnitude $\sqrt{J(J+1)}$, where J is a total angular momentum quantum number that takes all values from $|L + S|$ to $|L - S|$ in integer steps. According to the uncertainty principle, $\vec{J}^*$ must precess about a fixed axis in space and only its projection J on this axis is truly constant; the vector projections L and S precess slowly about this axis at an angular velocity that increases with the strength of the coupling between spin and orbital momentum. The energy change that results from this weak coupling is taken to be proportional to the vector product of the magnetic moment associated with total spin and the magnetic field associated with the total orbital momentum or, in other words, to the vector product $\vec{S}^* \cdot \vec{L}^*$ given by an equation similar to (7.56):

$$|\Delta E| \quad \alpha \quad 2\vec{S}^* \cdot \vec{L}^* = J(J+1) - L(L+1) - S(S+1) \tag{7.64}$$

The relative spacing between energy levels given by equation (7.64) is known as the Landé interval rule. Whether the energy shift is positive or negative depends on averaged quantities such as equation (7.58).

The coupling model above is known as Russell-Saunders or *LS* coupling. For heavy elements, the spin-orbit coupling increases as the fourth power of nuclear charge (see problem 7.6) and can exceed the Coulomb interaction perturbation. This may be considered a consequence of the large electron velocities that occur near the nuclear center. When the velocity becomes an appreciable fraction of the limiting velocity c, the magnetic fields experienced by the electron are very strong (see eq. (7.49)). In this case, each electron spin couples strongly with the electron's own orbital momentum to form a resultant angular momentum quantum number j:

$$j = |l \pm s| \tag{7.65}$$

The total angular momentum quantum number J is then a sum of projections of the individual j_i on the steady axis of precession:

$$J = \sum_i j_i \cos \gamma_i \tag{7.66}$$

Where again the projections $j_i \cos \gamma_i$ take only values between j_i and $-j_i$ in integer steps. This type of coupling that occurs in heavy atoms is known as j - j coupling. As the reader can readily imagine, intermediate weight atoms exhibit a kind of mixed coupling where the different coupling energies are roughly equal, and none of the angular momentum components are even approximately constant, except for the total. (The complex exchange of angular momenta that occurs in this case is analogous to asymmetric tops when the moments of inertia are all sizable and unequal.)

In light atoms, the Coulomb and exchange integral corrections treated in the last section establish the pattern of energy levels; the angular momentum coupling produces a small splitting of otherwise multiply degenerate spin states in accord with the Landé interval rule (eq. (7.64)). Deviations from the Landé interval rule indicate that the simple *LS* coupling approximation is breaking down. The energy levels are still relatively easy to classify so long as the multiplet splitting is less than the exchange effect. However, eventually, in heavier atoms the j - j coupling predominates and the different multiplet states become intermingled with levels of other electron configurations; in this case, identification of levels is much more laborious. A more complete discussion of *LS* and j - j coupling and rules for multiplet splitting has been published by Condon and Shortley (ref. 8).

7.7 *LS* COUPLED ELECTRON CONFIGURATIONS

Electron configurations can be represented in various ways. One way is to designate for each electron the total quantum number n, the orbital quantum number l, the magnetic quantum number m (i.e., the projection of l on some fixed axis), and the spin state s. The total configuration for a multi-electron system might thus be expressed as

$$(n_1 l_1 m_1 s_1)(n_2 l_2 m_2 s_2) . . .$$

However, where LS coupling is a reasonably good approximation, a more meaningful notation is to designate the quantities that are approximately constant, namely, the total orbital momentum quantum number L, the total spin quantum number S, and the total angular momentum quantum number J. By convention, the electronic configuration is described by a term of the form

$$^{(2S+1)}L_J$$

The orbital momentum L is designated by capital letters S, P. D, F, G,. . . depending on whether L is 0, 1, 2, 3, 4,. . ., respectively. This notation obviously follows the conventions developed for single-electron spectra. The capital letters signify that the total orbital momentum for all the electrons is described. The superscript $2S + 1$ and subscript J are integers or half-integers that describe the units of total spin and total coupled orbital-spin momentum, respectively; $2S + 1$ is used rather than S because it describes the multiplicity of levels with nearly the same energy observed for light atoms by the spectroscopist. The total degeneracy of a given LS configuration is

$$g = (2S + 1)(2L + 1) = \sum_J (2J + 1) \tag{7.67}$$

Some general rules for the relative energy of the different LS coupled configurations can be formulated, but occasional exceptions to these rules are observed. The configuration with the maximum total spin, S, normally takes the lowest energy. Next the configurations with the maximum orbital momentum, L, usually take the lowest energy. Finally, the spin orbit coupling can have either a positive or negative coefficient in the Landé interval rule as discussed previously. Usually, the lowest value of J has the lowest energy in atoms with incomplete outer electron shells, (i.e., a positive coefficient occurs for the Landé interval rule), but the order reverses as the outer electron shell fills (a negative coefficient then occurs for the Landé interval rule).

The Pauli exclusion principle places some restrictions on the ways angular momenta can couple. For this reason, we must consider some differences between equivalent and nonequivalent electrons before classifying the levels for specific atoms. Equivalent electrons are those electrons with the same total quantum number n and the same orbital angular momentum quantum number l; they may take the same or different magnetic quantum numbers m and spin state s. However, according to the Pauli principle, equivalent electrons cannot simultaneously take the same magnetic and spin states. Nonequivalent electrons are those with different total quantum numbers n; these electrons may take the same or different values of l, m, and s without violating the Pauli principle, of course. As an example, consider two equivalent p electrons with quantum number n, that is, the configuration $(np)^2$. There are 15 different assignments of the magnetic quantum numbers m and the spin quantum states (α or β) allowed by the Pauli exclusion principle in this case. These are listed in the first three columns in table 7.2. The sum of the projections m and of the spin quantum numbers ±1/2 are shown in the next two columns of the table. These are related to the total L and S values as suggested in the last column. However, the one-to-one correspondence shown is

TABLE 7.2.- EQUIVALENT ELECTRON $(np)^2$ CONFIGURATIONS

Index	m			$\sum m$	$\sum s$	LS coupling notation
	1	0	-1			
1		$\alpha\beta$		0	0	$^1S_0$
2	$\alpha\beta$			2	0	$^1D_2$
3	α	β		1	0	
4	α		β	0	0	
5		α	β	-1	0	
6			$\alpha\beta$	-2	0	
7	α	α		1	1	$^3P_{2,1,0}$
8	β	α		1	0	
9	β	β		1	-1	
10	α		α	0	1	
11	β		α	0	0	
12	β		β	0	-1	
13		α	α	-1	1	
14		β	α	-1	0	
15		β	β	-1	-1	

somewhat misleading; configurations 3 and 8 and 5 and 14 should really be considered mixed ^1D and ^3P states, while 1, 4, and 11 are mixed ^1S, ^1D, and ^3P states; or, conversely, the ^1S state is a mixture of configurations 1, 4, and 11, etc. The one-to-one correspondence shown merely emphasizes that the correct number of degenerate states has been accounted for. The appearance of mixed states when the coordinate system or nomenclature is changed is common in quantum mechanics; it reflects the fact that the set of eigenfunctions chosen to represent the allowed set of quantum states is not unique. Any set can be expressed as a linear combination of eigenfunctions belonging to an equivalent set. For example, eigenfunctions in Cartesian coordinates can be expressed as a linear combination of eigenfunctions in spherical coordinates. Similarly, the ^1S, ^1D, and ^3P states in table 7.2 represent linear combinations of $(np\ ms)$ $(n\ p\ m'\ s')$ configurations. The main point is that no states with $\Sigma m = 2$ and $\Sigma s = 1$ can exist according to the Pauli principle, and so the D state must be a singlet. However, a state with $\Sigma m = 1$ and $\Sigma s = 1$ does exist, which requires that a ^3P state exist. Finally, the remaining number of configurations are all required to account for the total degeneracy of the ^1S, ^1D, and ^3P states; in other words, all possible states have been accounted for and the ^1P states, as well as the ^3S and ^3D states, do not result from the $(np)^2$ equivalent electron configurations.

The triplet ^3P states would normally be expected to have the lowest energy of all the $(np)^2$ configurations because they have the maximum total spin value S. The two equivalent p electron situation is characteristic of an incomplete electron shell, in which case the Landé interval rule coefficient would likely be positive and the triplet level energies would increase in the order $^3P_0$, $^3P_1$, and $^3P_2$. Of the two singlet states, the $^1D_2$ configuration would normally take the lowest energy because it has the higher total angular momentum value L.

Consider next the nonequivalent electron configurations, such as $(np)(n'p)$, where the principle quantum number is different. In this case, the spins can be equivalent and the principle quantum numbers can be exchanged to provide additional allowed states, as shown in table 7.3. The first 15 configurations are the same as in table 7.2, only a somewhat more concise notation $(n, l, m, s)(n', l', m', s')$ has been used to show the principle quantum numbers more easily. These are assigned the same one-to-one correspondence with ^1S, ^1D, and ^3P states as in table 7.2, again with the understanding that these states really represent mixed one-electron configurations. The remaining 21 configurations that appear when equivalent spin states and exchange of principle quantum numbers are accounted for are all needed to match the total degeneracy of ^1P, ^3S, and ^3D states not allowed in the equivalent electron case.

A similar procedure may be followed to determine the allowed states of LS coupling for other equivalent electron configurations (ref. 9). These are listed in table 7.4 for configurations s^2, p^2 through p^6, and d^2 through d^{10}. Note that a closed shell of electrons always yields the ^1S state; also n equivalent electrons give the same set of states as the closed shell less n electrons. Since any filled subshell of electrons contributes zero spin momentum and zero orbital momentum, the configuration $(s)^2(p)^n$ has the same terms as those listed for $(p)^n$; the configuration $(s)^2(p)^6(d)^n$ has the same terms as those listed for $(d)^n$, etc.

Ground state atoms of light elements consist of completed subshells and one partly filled subshell of equivalent electrons, and thus have terms such as given in table 7.4. Excited state atoms usually consist of one electron in an excited quantum state coupled to a core of ground state equivalent electron subshells. The orbital momentum and the spin of the excited electron are coupled to the core values in all possible ways to give the resultant term symbols. For example, consider the configuration $(np)^2(n'p)$. This may lead to the following terms (the core configuration term is given inside the square brackets):

$$(np)^2[^3P](n'p) \rightarrow {}^4D, {}^4P, {}^4S, {}^2D, {}^2P, {}^2S$$

$$(np)^2[^1D](n'p) \rightarrow {}^2F, {}^2D, {}^2P$$

$$(np)^2[^1S](n'p) \rightarrow {}^2P$$

TABLE 7.3.- NONEQUIVALENT ELECTRON $(np)(n'p)$ CONFIGURATIONS

Index	Configuration	$\sum m$	$\sum s$	*LS* coupling notation
1	$(n,1,0,\alpha)(n',1,0,\beta)$	0	0	$^1S_0$
2	$(n,1,1,\alpha)(n',1,1,\beta)$	2	0	$^1D_2$
3	$(n,1,1,\alpha)(n',1,0,\beta)$	1	0	
4	$(n,1,1,\alpha)(n',1,-1,\beta)$	0	0	
5	$(n,1,0,\alpha)(n',1,-1,\beta)$	-1	0	
6	$(n,1,-1,\alpha)(n',1,-1,\beta)$	-2	0	
7	$(n,1,1,\alpha)(n',1,0,\alpha)$	1	1	$^3P_{2,1,0}$
8	$(n,1,1,\beta)(n',1,0,\alpha)$	1	0	
9	$(n,1,1,\beta)(n',1,0,\beta)$	1	-1	
10	$(n,1,1,\alpha)(n',1,-1,\alpha)$	0	1	
11	$(n,1,1,\beta)(n',1,-1,\alpha)$	0	0	
12	$(n,1,1,\beta)(n',1,-1,\beta)$	0	-1	
13	$(n,1,0,\alpha)(n',1,-1,\alpha)$	-1	1	
14	$(n,1,0,\beta)(n',1,-1,\alpha)$	-1	0	
15	$(n,1,0,\beta)(n',1,-1,\beta)$	-1	-1	
16	$(n',1,1,\alpha)(n,1,0,\beta)$	1	0	$^1P_1$
17	$(n',1,1,\alpha)(n,1,-1,\beta)$	0	0	
18	$(n',1,0,\alpha)(n,1,-1,\beta)$	-1	0	
19	$(n,1,0,\alpha)(n',1,0,\alpha)$	0	1	$^3S_1$
20	$(n',1,0,\alpha)(n,1,0,\beta)$	0	0	
21	$(n,1,0,\beta)(n',1,0,\beta)$	0	-1	
22	$(n,1,1,\alpha)(n',1,1,\alpha)$	2	1	$^3D_{3,2,1}$
23	$(n',1,1,\alpha)(n,1,1,\beta)$	2	0	
24	$(n,1,1,\beta)(n',1,1,\beta)$	2	-1	
25	$(n',1,1,\alpha)(n,1,0,\alpha)$	1	1	
26	$(n',1,1,\beta)(n,1,0,\alpha)$	1	0	
27	$(n',1,1,\beta)(n,1,0,\beta)$	1	-1	
28	$(n',1,1,\alpha)(n,1,-1,\alpha)$	0	1	
29	$(n',1,1,\beta)(n,1,-1,\alpha)$	0	0	
30	$(n',1,1,\beta)(n,1,-1,\beta)$	0	-1	
31	$(n',1,0,\alpha)(n,1,-1,\alpha)$	-1	1	
32	$(n',1,0,\beta)(n,1,-1,\alpha)$	-1	0	
33	$(n',1,0,\beta)(n,1,-1,\beta)$	-1	-1	
34	$(n,1,-1,\alpha)(n',1,-1,\alpha)$	-2	1	
35	$(n',1,-1,\alpha)(n,1,-1,\beta)$	-2	0	
36	$(n,1,-1,\beta)(n',1,-1,\beta)$	-2	-1	

TABLE 7.4.- EQUIVALENT ELECTRON TERMS

Configuration	Term symbols
$(s)^1$	^2S
$(s)^2$	^1S
$(p)^1, (p)^5$	^2P
$(p)^2, (p)^4$	$^1S, ^1D, ^3P$
$(p)^3$	$^2P, ^2D, ^4S$
$(p)^6$	^1S
$(d)^1, (d)^9$	^2D
$(d)^2, (d)^8$	$^1S, ^1D, ^1G, ^3P, ^3F$
$(d)^3, (d)^7$	$^2P, ^2D, ^2D, ^2F, ^2G, ^2H, ^4P, ^4F$
$(d)^4, (d)^6$	$^1S, ^1S, ^1D, ^1D, ^1F, ^1G, ^1G, ^1I, ^3P, ^3P, ^3P, ^3F, ^3F, ^3G, ^3H, ^5D$
$(d)^5$	$^2S, ^2P, ^2D, ^2D, ^2D, ^2F, ^2F, ^2G, ^2G, ^2H, ^2I, ^4P, ^4D, ^4F, ^4G, ^6S$
$(d)^{10}$	^1S

7.8 EXAMPLES OF *LS* COUPLING

Several of the light atoms provide good examples of *LS* coupling. Some are listed in table 7.5 with their ground state configuration and a few of their lower-lying excited states. The energy levels are taken from Moore (ref. 10); small uncertainties in the absolute value for some metastable levels are not indicated.

The ground state of neutral helium, He I, consists of two equivalent $(1s)$ electrons. This constitutes a closed shell and can have only the ^1S configuration. Since both spin and orbital momentum are zero, the total angular momentum J must be zero. The excited state $(1s)(2s)$ configuration lies lower than the $(1s)(2p)$ configuration since the $(2s)$ electron is shielded less effectively from the nuclear charge by the remaining $(1s)$ electron than is the $(2p)$ electron. The electrons with different total quantum number are nonequivalent and the spins can now add up to either triplet or singlet states. The total angular momentum of the S states equals the spin, of course, but the J values for the ^3P state can be 2, 1, or 0: the three ways a spin of one can add to one unit of orbital momentum. The superscript o on the $^3P^0$ and $^1P^0$ states signifies that an odd number of orbital angular momentum quanta occurs in the configuration. The absence of this superscript signifies an even number. This notation is convenient for spectroscopic purposes because the strong (electric dipole) optical transitions for *LS* coupled atoms occur only between even and odd states.

The levels of Li I are similar to the hydrogen levels (problem 7.6), except that some extra levels occur because of the greater degeneracy of states available to the outer electron. Li II is isoelectronic with He I and has a similar set of levels, but with lower energies because of the greater nuclear charge.

TABLE 7.5.- LOW-LYING ELECTRONIC STATES OF LIGHT ATOMS

Atom	Configuration	Term	Energy, cm^{-1}
He I	$(1s)^2$	${}^1S_0$	0
	$(1s)(2s)$	${}^3S_1$	159850.32
	"	${}^1S_0$	166271.70
	$(1s)(2p)$	${}^3P^0_2$	169081.11
	"	${}^3P^0_1$	169081.19
	"	${}^3P^0_0$	169082.18
	"	${}^1P^0_1$	171129.15
Li I	$(1s)^2(2s)$	${}^2S_{1/2}$	0
	$(1s)^2(2p)$	${}^2P^0_{1/2}$	14903.66
	"	${}^2P^0_{3/2}$	14904.00
	$(1s)^2(3s)$	${}^2S_{1/2}$	27206.12
	$(1s)^2(3p)$	${}^2P^0_{1/2}$	30925.38
	"	${}^2P^0_{3/2}$	
	$(1s)^2(3d)$	${}^2D_{3/2}$	31283.08
	"	${}^2D_{5/2}$	31283.12
Be I	$(1s)^2(2s)^2$	${}^1S^0_0$	0
	$(1s)^2(2s)[{}^2S](2p)$	${}^3P^0_0$	21979.4
	"	${}^3P^0_1$	21980.1
	"	${}^3P^0_2$	21982.5
	"	${}^1P^0_1$	42565.3
	$(1s)^2(2s)[{}^2S](3s)$	${}^3S_1$	52082.1
	"	${}^1S_0$	54677.2
B I	$(1s)^2(2s)^2[{}^1S](2p)$	${}^2P^0_{1/2}$	0
	"	${}^2P^0_{3/2}$	16
	$(1s)^2(2s)(2p)^2$	${}^4P_{1/2}$	28805
	"	${}^4P_{3/2}$	28810
	"	${}^4P_{5/2}$	28816
	$(1s)^2(2s)^2[{}^1S](3s)$	${}^2S_{1/2}$	40040
	$(1s)^2(2s)(2p)^2$	${}^2D_{5/2}$	47857
	"	${}^2D_{3/2}$	

TABLE 7.5.- LOW-LYING ELECTRONIC STATES OF LIGHT ATOMS - Continued

Atom	Configuration	Term	Energy, cm^{-1}
C I	$(1s)^2(2s)^2(2p)^2$	$^3P_0$	0
	"	$^3P_1$	16.4
	"	$^3P_2$	43.5
	"	$^1D_2$	10193.7
	"	$^1S_0$	21648.4
	$(1s)^2(2s)(2p)^3$	$^5S^0_2$	33735.2
	$(1s)^2(2s)^2(2p)[^2P^0](3s)$	$^3P^0_0$	60338.8
	"	$^3P^0_1$	60353.0
	"	$^3P^0_2$	60393.5
	"	$^1P^0_1$	61982.2
	$(1s)^2(2s)(2p)^3$	$^3D^0_3$	64088.6
	"	$^3D^0_2$	64093.2
	"	$^3D^0_1$	64092.0
N I	$(1s)^2(2s)^2(2p)^3$	$^4S^0_{3/2}$	0
	"	$^2D^0_{5/2}$	19223
	"	$^2D^0_{3/2}$	19231
	"	$^2P^0_{3/2}$	28840
	"	$^2P^0_{1/2}$	
	$(1s)^2(2s)^2(2p)^2[^3P](3s)$	$^4P_{1/2}$	83285.5
	"	$^4P_{3/2}$	83319.3
	"	$^4P_{5/2}$	83366.0
	"	$^2P_{1/2}$	86131.4
	"	$^2P_{3/2}$	86223.2
O I	$(1s)^2(2s)^2(2p)^4$	$^3P_2$	0
	"	$^3P_1$	158.5
	"	$^3P_0$	226.5
	"	$^1D_2$	15867.7
	"	$^1S_0$	33792.4
	$(1s)^2(2s)^2(2p)^3[^4S^0](3s)$	$^5S^0_2$	73767.8
	"	$^3S^0_1$	76794.9

TABLE 7.5.- LOW-LYING ELECTRONIC STATES OF LIGHT ATOMS - Concluded

Atom	Configuration	Term	Energy, cm^{-1}
O I	$(1s)^2(2s)^2(2p)^3[^4S^0](3p)$	$^5P_1$	86625.4
	"	$^5P_2$	86627.4
	"	$^5P_3$	86631.0
	"	$^3P_2$	88630.8
	"	$^3P_1$	88630.3
	"	$^3P_0$	88631.0
	$(1s)^2(2s)^2(2p)^3[^4S^0](4s)$	$^5S^0_2$	95476.4
	"	$^3S^0_1$	96225.5
F I	$(1s)^2(2s)^2(2p)^5$	$^2P^0_{3/2}$	0
	"	$^2P^0_{1/2}$	404.0
	$(1s)^2(2s)^2(2p)^4[^3P](3s)$	$^4P_{5/2}$	102406.5
	"	$^4P_{3/2}$	102681.2
	"	$^4P_{1/2}$	102841.2
	"	$^2P_{3/2}$	104731.9
	"	$^2P_{1/2}$	105057.1
Ne I	$(1s)^2(2s)^2(2p)^6$	$^1S_0$	0
	$(1s)^2(2s)^2(2p)^5[^2P_{3/2}](3s)$	$[3/2]^0_2$	134043.8
	"	$[3/2]^0_1$	134461.2

The terms of Be I are similar to He I, except that again some extra levels occur because of the greater degeneracy of states available to the outer electron, such as the levels of the $(1s)^2(2s)(2p)$ configuration. When the interaction between the outer electron and the core of inner electrons is weak, a term specifying total spin and angular momentum of the core electrons can be assigned. In the present case, the core of $(1s)^2(2s)$ electrons can only take one term, the ^2S. However, when cores involve several p electrons, several core terms with different energy levels are possible. Be II is isoelectronic with Li I and has a similar set of energy levels, while Be III has a He I-like set of energy levels.

B I has one unpaired $(2p)$ electron in the ground state and so gives rise to a close-lying doublet of ^2P states. The first excited level occurs by promoting one of the $(2s)$ electrons to the $(2p)$ orbit. The two equivalent p electrons can couple in the ^3P, ^1D, or ^1S term configurations as indicated in table 7.4; coupling the $(2s)$ electron to these configurations leads to ^4P, ^2P, ^2D, and ^2S terms. Of these, the term ^4P with greatest degeneracy is lowest, next is the doublet term ^2D with greatest orbital momentum. This sequence is interrupted by the $(1s)^2(2s)^2(3s)$ excited state and the ^2P and ^2S levels are not observed in B I. However, all these levels are observed below the $(1s)^2(2s)^2(3s)$ excited level in the isoelectronic sequence C II.

C I has the set of terms given in table 7.4 for two equivalent p electrons. Again, the terms with greatest multiplicity are lowest in energy and, of those with the same multiplicity, the terms with largest orbital momentum are lowest. Like B I, the first excited level occurs when one of the $(2s)$ electrons is promoted to $(2p)$. This gives rise to a sequence of terms that couples the remaining $(2s)$ electron to the terms of three equivalent p electrons, namely, ^5S, ^3D, ^3P, ^1D, ^3S, and ^1P. This sequence is interrupted by the $(1s)^2(2s)^2(2p)(3s)$ levels in C I; the first four terms of the sequence appear in N II before the $(3s)$ excited state and the complete sequence is unbroken in O III.

In N I, the ground state terms comprise the set for three equivalent p electrons as given in table 7.4. The state of greatest multiplicity, ^4S, is lowest. Of the doublet states, the ^2D state with greatest orbital momentum is lowest. When one of the electrons is excited to the $(3s)$ state or higher, the core of two equivalent p electrons can take the terms ^3P, ^1D, or ^1S, but as indicated in table 7.4 the lowest of these is the ^3P core state, just as for the ground state of C I. The ^1D core state has been identified in some of the higher excited levels.

The ground levels for O I comprise the set of terms given in table 7.4 for four equivalent p electrons. The lowest of these is the ^3P state with the greatest multiplicity and, of the singlet states, the ^1D state with greatest orbital momentum is lowest. When one of the outer electrons is excited, the core can take ^4S, ^2D, and ^2P configurations with the lowest of these the ^4S, just as for N I. The remaining two core configurations give rise to a series of identified levels that for highly excited states lie above the ionization limit for the ^4S core state of O I.

F I in the ground state has only the one ^2P term allowed for five equivalent p electrons. When one of these is promoted to an excited level, the lowest-lying core configuration is ^3P, as for the ground state of O I. Ne I has a closed shell in the ground state and so has the term ^1S; both the spins and angular momenta are all paired in this case. In excited states, the *LS* coupling approximation becomes rather poor for Ne, and the *LS* term symbols are abandoned in favor of a simple number that designates the coupling of the orbital momentum of the excited electron with the total angular momentum of the core (called j,l coupling); then the total angular momentum J is the coupling between the j,l value and the spin of the excited electron, ±1/2.

7.9 DIATOMIC MOLECULE ELECTRONIC STATES

At temperatures where electronic states become excited to an appreciable extent, polyatomic molecules generally dissociate. However, many diatomic molecules are rather strongly bound and excited states of these molecules are often observed. The important characteristic so far as the degeneracy of any molecular state is concerned is the symmetry, and the symmetry of diatomic molecules is cylindrical. An electron subject to a purely cylindrical force field would retain constant angular momentum about the axis of symmetry and constant linear momentum along the axis of symmetry. The diatomic molecule has very strong fields at the ends of the molecule, of course, which cause large changes in the total angular momentum as the electron reflects from these regions; but because of the overall cylindrical symmetry, the angular momentum about the cylindrical axis is preserved. If there were no spin-orbital coupling with other electrons, this component of angular momentum would be conserved for each individual electron. With coupling, the individual electrons may change angular momentum, but the total angular momentum about the cylindrical axis is conserved. For a molecule of light atoms, the coupling is weak and a situation occurs somewhat similar to *LS* coupling in atoms. Typically, the orbital momenta of the individual electrons add to form a total component of orbital momentum which has a relatively constant component along the molecular axis of symmetry and which precesses about this axis so that the time average of the component orthogonal to this axis vanishes. Similarly, the spin of the individual electrons may add to form a total spin that also takes a relatively constant component along the molecular axis of symmetry and precesses about this axis. The constant components of electronic angular momentum then couple with the angular momentum of the nuclear rotations to give a total angular momentum, exclusive of the nuclear spin angular momentum. Other coupling schemes sometimes occur in which different components are the relatively constant ones; these are discussed briefly after a review of the spectroscopic notation used to describe the various coupling schemes.

The notation chosen to describe diatomic molecular momentum states is patterned after the atomic *LS* coupled states. Greek letters are used in place of English; small Greek letters σ, π, δ, . . . signify 0, 1, 2, . . ., quanta of angular momenta about the cylindrical axis for the individual electrons. Capital Greek letters Σ, Π, Δ, . . . specify the total orbital momentum of all electrons along the internuclear axis; the spins add up algebraically just as for atoms. A difference between the degeneracies for the cylindrical and spherical systems does occur. The Σ term has no component of angular momentum along the internuclear axis and is a singlet state. However, the Π, Δ, and higher angular momentum states all have a doubling of levels corresponding to either clockwise or counterclockwise angular momentum about the cylindrical axis. The spherically symmetric case had larger degeneracies than this because of the additional symmetry involved (recall that S, P, D, states of the atoms have degeneracies 1, 3, 5, . . .). Thus, in the cylindrically symmetric case, the Pauli exclusion principle limits the σ state to two electrons and the π, δ, etc., states to four electrons each.

The total spin momentum S can couple with the total orbital momentum Λ in $2S + 1$ different ways as before, and the molecular term is designated $^{2S+1}\Lambda$ where Λ represents one of the letters Σ, Π, Δ, etc. The degeneracy of this term is $(2S + 1)$ if $\Lambda = \Sigma$, $2(2S + 1)$ if Λ takes any of the other values.

Some additional elements of nomenclature are worth mentioning: Σ states are often given a superscript + or -, that is, Σ^+ or Σ^-, depending on whether the total electronic wave function is even or odd with respect to a plane including the axis of symmetry. The ± symmetry is always present in states with $\Lambda \neq 0$, so the notation is redundant and is therefore omitted in this case. For example, the steady-state symmetrical wave function with $\Lambda \neq 0$ can be represented as the sum

$$\psi_+ = e^{i\Lambda\phi} + e^{-i\Lambda\phi}$$

and the steady state unsymmetrical wave function as the difference

$$\psi_- = e^{i\Lambda\phi} - e^{-i\Lambda\phi}$$

where ϕ is the angle in cylindrical coordinates. The Σ states can be compounded of π, δ, etc., electrons and so can have this even and odd symmetry with respect to ϕ, even though the total angular momentum is zero.

A subscript g or u (gerade of ungerade) is also used to represent the fact that the electronic wave function is even or odd with respect to the plane bisecting the nuclear axis. This notation is required only if the diatomic molecule is homonuclear, that is, composed of atoms of equal nuclear charge; this symmetry is destroyed otherwise.

English letters X, A, B, C, . . ., a, b, c, . . ., etc. often precede the term symbol for molecular states. The capital letters A, B, C, . . . designate a sequence of excited states having the same multiplicity, and the lower case letters a, b, c, . . . designate another sequence with different multiplicity. Usually, the lower case letters are assigned to the lowest multiplicity and the capital letters to the higher multiplicity. The ground state is designated by X regardless of its multiplicity. (Much of the spectroscopic notation was assigned before the classification with theoretical quantum models was understood and, therefore, occasional exceptions to the conventions above occur. Sometimes the sequence of levels is not in correct alphabetical order, and the multiplicities may not coordinate properly with the capital and lower case notations.) Sometimes a value of Ω, the total component of electronic angular momentum along the internuclear axis, is given as a subscript to the term symbol. This component is usually an algebraic sum of the orbital component Λ and the spin component Σ along the axis. However, the value of Ω is not always known from an analysis of the spectra; the molecular spectra are not generally as well ordered in their classification as atomic spectra.

Some examples of molecular energy levels are given in table 7.6 (refs. 11,12). Note that the degeneracies are all $2(2S + 1)$ except the Σ states, where they are $(2S + 1)$. In calculating the partition function for N_2, we can normally

TABLE 7.6.- SOME DIATOMIC MOLECULE ELECTRONIC STATES

Molecule	Term	Energy, cm^{-1}	Degeneracy, g
N_2	$X^1\Sigma_g^+$	0	1
	$A^3\Sigma_u^+$	50206	3
	$B^3\Pi_g$	59626	6
	$C^3\Pi_u$	89147	6
	$a^1\Pi_g$	69290	2
O_2	$X^3\Sigma_g^-$	0	3
	$a^1\Delta_g$	7918	2
	$b^1\Sigma_g^+$	13195	1
	$A^3\Sigma_u^+$	36096	3
	$B^3\Sigma_u^-$	49802	3
NO	$X^2\Pi_{1/2}$	0	2
	$X^2\Pi_{3/2}$	121	2
	$A^2\Sigma^+$	43966	2
	$B^2\Pi$	45930	4
	$C^2\Sigma^+$	52148	2
	$D^2\Sigma^+$	53083	2
	$E^2\Sigma^+$	60628	2

neglect all but the ground state because the other states are high enough in energy that N_2 is all dissociated before the electronic states are significantly populated, except at very high pressure of 100 atm or greater. However, where radiation is concerned, even lightly populated excited states must be accounted for because $B \rightarrow A$ and $C \rightarrow B$ transitions (1st and 2nd positive band systems of N_2, respectively) are very strong radiators.

Oxygen, on the other hand, has two low-lying excited levels that must be accounted for in the partition function. Also, the $B^3\Sigma_u^-$ level must be accounted for in radiation calculations even when weakly populated because the $B \leftrightarrow X$ transitions are the Schumann-Runge bands, one of the strongest absorbers and radiators in the ultraviolet.

Finally, for NO, note that the ground state is split by spin-orbit coupling into two close levels that have been identified. There are just two states for each value of Ω because of the cylindrical symmetry rather than $2J + 1$ as for the spherically symmetric atom, corresponding to the projections $\pm\Omega$ along the axis of symmetry. Since NO is heteronuclear, the g and u notations do not appear, of course.

In addition to the coupling between orbital and spin motion of the electrons, the angular momentum of electronic motion is coupled to the angular momentum of the nuclear rotations in the molecule to give the total angular momentum J. Strictly speaking, this coupling should include the spin angular momentum of the nuclei also. However, the coupling with nuclear spin is found to be so weak that it does not normally produce observable fine structure. Thus nuclear spin is normally considered to merely shift the zero point energy and the zero point entropy (as discussed in ch. 4). By convention, the so-called "total" angular momentum J is taken to represent just the total of the coupled electronic angular momentum and the angular momentum associated with the rotations of the molecular structure of atomic nuclei. Several different coupling schemes may occur, depending on the relative strength of the coupling coefficients involved. These different coupling models are referred to as Hund's coupling cases (a), (b), (c), (d), and (e) (refs. 11 and 12). Only the first four have any practical importance, that is, they approximately describe molecular states actually observed. Case (e) describes a limiting case that is possible in principle but not observed. Briefly, the four cases may be described as follows:

Case (a). The coupling between nuclear rotational angular momentum N and the electronic motion is very weak. However, the coupling between the electronic motion and the nuclear axis is strong, that is, the axial component of orbital angular momentum Λ and the axial component of the spin angular momentum Σ are strongly coupled to give a resultant Ω that is relatively constant. The components N and Ω then couple to give a resultant total angular momentum J that is constant in magnitude and direction; J takes values Ω, $\Omega + 1$, $\Omega + 2$, etc. The N and Ω components precess about the vector J, while L and S, the total electronic orbital and spin angular momenta, respectively, precess about the nuclear axis with constant axial components Λ and Σ. The total angular momentum is related to N and Ω by

$$J(J + 1) = N^2 + \Omega^2$$

so the rotational energy associated with the nuclear rotations is given by expressions such as

$$E_r = B[J(J + 1) - \Omega^2]$$

Case (b). When $\Lambda = 0$ and $S \neq 0$, the spin S is not coupled to the internuclear axis at all and Ω is not well defined. Sometimes even if $\Lambda \neq 0$, S may be so weakly coupled that Hund's case (b) applies. In this case, Λ and N form a resultant designated by K, which takes values Λ, $\Lambda + 1$, $\Lambda + 2$, etc; K represents the total angular momentum except for electron spin:

$$K(K + 1) = N^2 + \Lambda^2$$

Then K and S couple to give a very weak splitting of levels. The nuclear rotational energy then takes the form

$$E_r = B[K(K + 1) - \Lambda^2]$$

if the small splitting of levels is neglected. Most molecules made up of light atoms are covered by Hund's cases (a) and (b).

Case (c). If a heavy atom is present in the molecule, Λ and Σ are not well defined, that is, the axial components of L and S are not very constant. In this case, L and S form a resultant J that then precesses about the nuclear axis with a constant component Ω. The component Ω couples with N to form the total J

$$J(J + 1) = N^2 + \Omega^2$$

which gives the same pattern of nuclear rotational levels as case (a).

Case (d). This case is approached in very highly excited electronic states where the outer electron is in a Bohr-like orbit. Then the energy is determined primarily by the total quantum number; orbital angular momentum and spin are very weakly coupled, just as for the H-atom levels in problem 7.6. In this case, the rotational fine structure results almost solely from the nuclear rotations.

$$E_r \simeq BR(R + 1)$$

By convention, the nuclear rotation quantum number is designated by R for this case (ref. 12). This case is not often observed in practice because, when excitation energies are sufficient to excite the upper Bohr orbits in a molecule, the molecule usually dissociates.

Case (e). In principle, one can conceive of a case in which L and S are strongly coupled, but where the resultant is weakly coupled to the nuclear rotations. This case does not seem to be observed (refs. 11, 12, and 13).

One can appreciate that the interpretation of molecular spectra with such coupling schemes is an important aid in untangling the fine structure of lines observed. Even where this fine structure does not exactly fit any one of the coupling schemes, it may be sufficiently close to one of them to allow classification of the levels observed. In this way, the degeneracies of the various levels may be assigned so that the thermodynamicist can proceed to calculate partition functions and thermodynamic properties.

Some ambiguity about the symbol J may occur because it is commonly used to represent the molecular rotational quantum number (as in ch. 4), but in discussing the coupling schemes, J is reserved to signify the "total" angular momentum quantum number (excluding nuclear spin momentum as discussed above) and the molecular rotational quantum numbers are designated by N (or R in Hund's cases (d) and (e)). In practice, this ambiguity does not cause much of a problem because the electronic angular momentum numbers are usually small compared with the molecular rotational quantum numbers of interest. Stable electronic structures tend to pair up spins and fill the lowest orbital momentum states so that the values of Σ and Λ are small, usually 0, 1/2, or 1. On the other hand, the most populated molecular rotational states, even at ordinary temperature, are those with N the order of 10 or greater. In this case, J and N are approximately equal and, to the approximation usually required to calculate partition functions, it is sufficient to treat the molecular rotations as though they are independent of coupling effects with electronic motion.

7.10 ELECTRONIC PARTITION FUNCTIONS

The electronic energy levels and degeneracies of atoms and molecules are observed to follow a very irregular pattern so that closed, analytic expressions for the electronic partition functions are not derivable. Fortunately, the energy levels are generally so widely spaced that only the first few terms of the series are required at normal temperatures. For example, the electronic partition functions given in table 7.7 for a few typical atomic species are carried out to energy levels E/k up to 100,000° K. Electronic levels

TABLE 7.7 SOME APPROXIMATE ELECTRONIC PARTITION FUNCTIONS FOR ATOMS AT TEMPERATURES BELOW 20,000° K

$$Q(H) = 2$$

$$Q(H^+) = 2$$

$$Q(N) = 4 + 10\, e^{-27,658/T} + 6\, e^{-41,495/T}$$

$$Q(N^+) = 1 + 3e^{-70.6/T} + 5\, e^{-188.9/T} + 5\, e^{-22,036/T} + e^{-47,030/T} + 5\, e^{-67,865/T}$$

$$Q(0) = 5 + 3e^{-228.9/T} + e^{-325.9/T} + 5\, e^{-22,830/T} + e^{-48,621/T}$$

$$Q(0^+) = 4 + 10\, e^{-35,589/T} + 6\, e^{-58,224/T}$$

$$Q(e) = 2$$

are typically so widely spread in this region that there is very little ambiguity about the cutoff level and, for many purposes, these expressions are adequate for temperatures up to about 20,000° K where higher-order terms are the order of e^{-5} or smaller. Molecules are usually dissociated into atoms above 10,000° K, so truncation of the partition functions at $E/k = 50{,}000°$ K is generally adequate for molecules. Table 7.8 gives some approximate molecular partition functions. The contribution of electronic energy to the thermodynamic functions can readily be computed from these expressions by taking the proper derivatives (as outlined in ch. 1):

TABLE 7.8.- SOME APPROXIMATE ELECTRONIC PARTITION FUNCTIONS FOR MOLECULES AT TEMPERATURES BELOW 10,000° K

$Q(N_2) = 1$
$Q(O_2) = 3 + 2\,e^{-11{,}393/T} + e^{-18{,}985/T}$
$Q(NO) = 2 + 2\,e^{-174.2/T}$
$Q(H_2) = 1$
$Q(Cl_2) = 1 + 6\,e^{-26{,}345/T}$
$Q(HCl) = 1$
$Q(N_2^{+}) = 2 + 4\,e^{-13{,}191/T} + 2\,e^{-36{,}634/T}$
$Q(O_2^{+}) = 4 + 8\,e^{-45{,}898/T} + 4\,e^{-55{,}818/T}$
$Q(NO^{+}) = 1 + 6\,e^{-57{,}984/T}$
$Q(O_2^{-}) = 4 + 4\,e^{-19{,}280/T} + 4\,e^{-34{,}819/T}$

$$Q_e = \sum_{n=0}^{m} g_n\, e^{-\varepsilon_n/kT} \tag{7.68}$$

$$\left(\frac{E - E_o}{RT}\right)_e = \left(\sum_{n=0}^{m} \frac{\varepsilon_n}{kT} g_n\, e^{-\varepsilon_n/kT}\right)\bigg/ Q_e \tag{7.69}$$

$$\left(\frac{C_v}{R}\right)_e = \left[\sum_{n=0}^{m} \left(\frac{\varepsilon_n}{kT}\right)^2 g_n\, e^{-\varepsilon_n/kT}\right]\bigg/ Q_e - \left(\frac{E - E_o}{RT}\right)_e^2 \tag{7.70}$$

$$\left(\frac{S}{R}\right)_e = \ln Q_e + \left(\frac{E - E_o}{RT}\right)_e \tag{7.71}$$

If higher-order terms are all included, the simple summation in equation (7.68) becomes divergent for all species at all temperatures. The electronic levels all become hydrogen-like when a single excited electron is promoted to very high quantum states because, far from the nucleus, the inner electrons serve merely to screen off the appropriate number of nuclear charges and the resultant field is like the spherical field from a point charge. Even molecular configurations of nuclei and surrounding inner electrons eventually act as a point charge. The hydrogen-like system is an exception in that simple mathematical expressions for the electronic degeneracies and energies exist:

$$Q_e = \sum_{n=1}^{\infty} 2n^2 \, e^{-E_1/n^2kT} \tag{7.72}$$

where $E_1 = -(Z - p)^2 e^2/2a$, Z is the nuclear charge, and p is the number of inner electrons (i.e., $Z - p = 1$ for neutral species, 2 for single ionized species, etc.). For very large n, the energy levels become so closely spaced that the summation of degeneracies involved diverges, as is shown by evaluating the remainder of the summation above some large quantum number m as an integral:

$$\begin{aligned} Q_e &= \sum_{n=1}^{m} 2n^2 \, e^{-E_1/n^2kT} + \int_m^{\infty} 2n^2 \, e^{-E_1/n^2kT} \, dn \\ &= \sum_{n=1}^{m} 2n^2 \, e^{-E_1/nkT} + \int_0^{m^{-2}} \frac{e^{-E_1x/kT} \, dx}{x^{5/2}} = \infty \end{aligned} \tag{7.73}$$

For more complex atoms and molecules, the first part of the summation changes, but at some level m the higher-order terms become hydrogen-like and the summation diverges at any temperature (eq. (7.73)). Fortunately, nature does not require that we live in an infinite entropy universe. The upper electronic levels are effectively truncated by collision-like perturbations due to nearest neighbors in any finite density matter, yielding a finite sum that depends on the density of neutral and/or ionized particles surrounding the atom. This effect is treated in more detail in chapter 8, which discusses several higher-order corrections to the simple, separable partition functions considered thus far.

7.11 CONCLUDING REMARKS

The contributions of electronic energy states to the partition functions and derivative thermodynamic properties usually cannot be expressed analytically, even in a first approximation, as could the contributions from rotational and vibrational modes of molecules. However, only the first few states need to be considered even at rather elevated gas temperatures; therefore, the problem is simply treated by truncating the partition function sum after the first few terms; experimental values are used for the energy levels while the degeneracies are deduced from a classification of the spectra in terms of multi-electron wave functions that have properties similar to products of one-electron wave functions. The necessary data are available for atoms and most common diatomic molecules. At temperatures where higher electronic states need to be considered, molecules usually dissociate and the atoms all become hydrogen-like. Little is known about electronic states of polyatomic molecules but, again, these usually dissociate at temperatures where electronic energy levels need to be considered, so the only data normally required to evaluate thermodynamic properties in this case are the ground state degeneracies.

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CHAPTER 8 - PARTITION FUNCTION CORRECTIONS

8.1 SUMMARY

The vibration-rotation interaction coupling in diatomic molecules is analyzed and first-order expressions for the energy levels are deduced. Corrections to the partition function to account for this coupling are derived.

The effects of long-range intermolecular forces due to induced dipole-induced dipole interactions, dipole-induced dipole interactions, charge-dipole interactions, and charge-charge interactions are considered. London's quantized oscillator model (ref. 1) of the induced dipole-induced dipole interaction is developed. The partition function including effects of such dispersion forces is derived and is shown to lead to the virial equation of state. For a model combining the hard sphere and long-range attractive type potentials, this is found to lead to the van der Waals equation of state. The equation of state near the critical point is presented in reduced form (thermodynamic variables expressed in units of critical point values).

Finally, approximate corrections to the electronic partition functions are derived to account for perturbations of excited electronic states induced by neighboring neutral particles, heavy ions, and fast electron collisions.

8.2 INTRODUCTION

Where good accuracy is required, several corrections to the partition function must be considered. Among the most important are corrections for vibration-rotation coupling, for intermolecular forces, and for neighboring atom perturbations that lower the effective ionization potential and truncate the electronic partition function. These three corrections are now considered.

8.3 VIBRATION-ROTATION COUPLING IN DIATOMIC MOLECULES

In chapter 4, the rotating diatomic molecule was treated as a rigid rotator. Now the centrifugal stretching of the internuclear bond which occurs as the body rotates is considered. A semiclassical derivation illustrates the physics involved, and is also sufficiently accurate for most purposes. The centrifugal force on the molecule may be expressed in terms of the angular momentum L or $\mu r^2 \omega_r$ as

$$F = \mu \omega_r{}^2 r = \frac{L^2}{\mu r^3} \tag{8.1}$$

This force is balanced by a restoring force derived from the internuclear potential, which for a harmonic potential is the familiar Hooke law, $\mu\omega_v^2(r - r_o)$, where ω_v is the vibrational circular frequency and r_o is the equilibrium internuclear distance for zero angular momentum:

$$\mu\omega_v^2(r - r_o) = \frac{L^2}{\mu r^3} \tag{8.2}$$

The energy is just the sum of rotational and potential energies:

$$E_r = \frac{\mu}{2}\omega_r^2 r^2 + \frac{\mu}{2}\omega_v^2(r - r_o)^2 = \frac{L^2}{2\mu r^2} + \frac{L^4}{2\mu^3\omega_v^2 r^6} \tag{8.3}$$

The interatomic distance r is now expanded in terms of the small difference $r - r_o$ as

$$\frac{1}{r^2} = \frac{1}{r_o^2\left(1 + \frac{r - r_o}{r_o}\right)^2} = \frac{1}{r_o^2}\left[1 - 2\left(\frac{r - r_o}{r_o}\right) + \ldots\right] \tag{8.4}$$

and, to terms of order L^4, the energy becomes

$$E_r = \frac{L^2}{2\mu r_o^2} - \frac{L^4}{2\mu^3\omega_v^2 r_o^6} + \ldots \tag{8.5}$$

The angular momentum L^2 can be replaced by its quantum value $J(J+1)\hbar^2$ to give

$$E_r = \frac{\hbar^2}{2\mu r_o^2} J(J+1) - \frac{\hbar^4}{2\mu^3\omega_v^2 r_o^6} J^2(J+1)^2 + \ldots \tag{8.6}$$

Compare this with the spectroscopist's notation,

$$E_r = BJ(J+1) - DJ^2(J+1)^2 + \ldots \tag{8.7}$$

to obtain expressions for B and D. The expansion can be carried out to third- and higher-order terms, but available experimental precision does not generally warrant fitting the data to more terms than presented above.

In addition to the average bond stretching, there is a dependence of B on the vibrational quantum level because $\langle r_o^{-2}\rangle$ is not the same as $\langle r_o^{-1}\rangle^2$. Let

$$r_o = r_e + \delta \sin \omega_v t \tag{8.8}$$

where δ is the amplitude of vibrational motion involved and r_e is the equilibrium interatomic distance when both rotations and vibrations are absent:

$$\left\langle \frac{1}{(r_e + \delta\ \sin\omega_v t)^2} \right\rangle = \frac{1}{r_e^2} \left\langle \left[1 - \frac{2\delta}{r_e} \sin\omega_v t + 3\left(\frac{\delta}{r_e}\right)^2 \sin^2\omega_v t + \ . \ . \ . \right] \right\rangle$$

$$= \frac{1}{r_e^2}\left[1 + \frac{3}{2}\left(\frac{\delta}{r_e}\right)^2 + \ . \ . \ . \right] \tag{8.9}$$

The vibrational amplitude δ is related to the vibrational quantum number v by equating the classical and quantum expressions for vibrational energy:

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega = \mu\omega^2 \frac{\delta^2}{2} \tag{8.10}$$

Thus for a purely harmonic oscillator the rotational energy constant B increases as the vibrational quantum number v increases:

$$B = B_e + \left(\frac{3\hbar^3}{2\mu^2\omega_v r_e^4}\right)\left(v + \frac{1}{2}\right) + \ . \ . \ . \tag{8.11}$$

Such an increase in B with vibrational quantum number is actually observed for some of the metal hydrides (LiH, KH, NaH, RbH, and CsH) in their excited $A^1\Sigma^+$ state, where the anharmonic cubic correction term $\omega_e x_e$ is negative - that is where the potential becomes steeper than quadratic as the molecule is stretched beyond the equilibrium position. However, for all other observed diatomic states, the anharmonic effects produce a shallower than quadratic potential as the molecule is stretched beyond the equilibrium position (i.e., $\omega_e x_e$ is positive), as shown in figure 8.1. In this case the average rotational constant corresponds to an internuclear distance that roughly bisects the potential turning points as suggested by the curve for $\bar{x}$ and thus B decreases as vibrational amplitude increases. Spectroscopists fit their data empirically to the relation

$$B = B_e - \alpha_e\left(v + \frac{1}{2}\right) + \gamma_e\left(v + \frac{1}{2}\right)^2 + \ . \ . \ . \tag{8.12}$$

Expressions for α_e can be derived if the form of the potential is known. For the Morse function, for example,

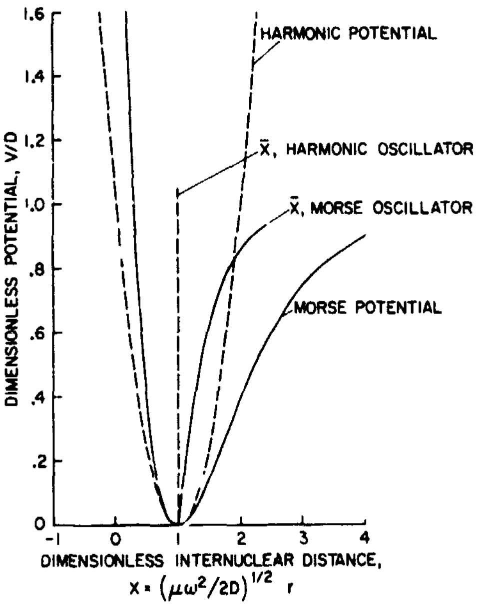

Figure 8.1.- Effects of anharmonicity on average internuclear distance.

$$\alpha_e = \frac{6\sqrt{\omega_e x_e B_e{}^3}}{\omega_e} - \frac{6B_e{}^2}{\omega_e} \tag{8.13}$$

The fundamental vibrational frequency is also affected by the rotations. The molecule may be considered to vibrate in an effective potential that is the sum of the vibrational potential $U_o(r)$ and the rotational energy:

$$U_{eff}(r) = U_o(r) + \frac{\hbar^2}{2\mu r^2} J(J + 1) \tag{8.14}$$

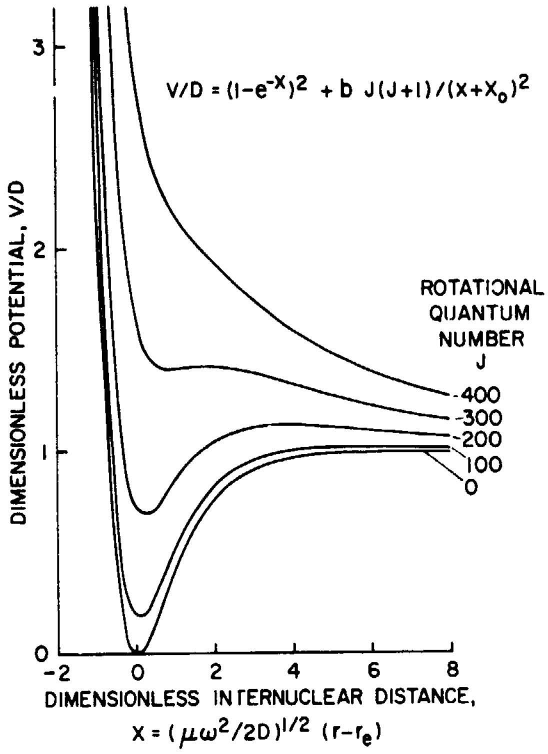

Figure 8.2.- Morse potential with rotational potential included, for N_2 $[b = (\hbar\omega/2D)^2 = 2.25\times10^{-4}$, $x_o = (\mu\omega^2 r_e{}^2/2D)^{1/2} = 3.5]$.

The effective potential is shown in figure 8.2 for a Morse oscillator and several rotational quantum numbers. One can see that the added "rotational potential" vanishes at large r, but grows important near r_e and actually creates a maximum in the effective potential. Eventually, at high enough rotational quantum numbers, the potential minimum disappears and the molecule dissociates by rotational stretching. The rotational contribution to the effective potential changes the shape about the minimum and so alters the vibrational frequency. When the interaction terms are derived for a given potential function, the results do not generally fit the experiments very well and, in practice, the energy levels for coupled vibration-rotation are simply fit to an expression of the form

$$E_{v,r} = B_e J(J + 1) - D_e J^2 (J + 1)^2 + \left(v + \frac{1}{2}\right)\omega_e - \left(v + \frac{1}{2}\right)^2 \omega_e x_e - \alpha_e \left(v + \frac{1}{2}\right)[J(J + 1)] + \ldots \tag{8.15}$$

For many purposes, the first-order correction terms given in equation (8.15), involving the coefficient D_e for centrifugal stretching, the coefficient $\omega_e x_e$ for anharmonicity, and the coefficient α_e for coupled rotation-vibration effects, are sufficient. The next order correction for anharmonicity, $[v + (1/2)]^3\omega_e y_e$, is typically the largest of the neglected terms in equation (8.15).

To derive an expression for the partition function, the energy relative to the ground state is needed (see eq. (1.72) in ch. 1). In this connection, the older spectroscopic energy expression given below in terms of integer quantum numbers is convenient because the ground state level is zero in this notation:

$$E_{vr} = B_0 J(J+1) - D_0 J^2 (J+1)^2 + \omega_0 v - \omega_0 x_0 v^2 - \alpha_0 v J(J+1) \tag{8.16}$$

where

$$\omega_0 = \omega_e(1 - x_e + \ldots) \qquad x_0 = x_e(1 + x_e + \ldots) \qquad B_0 = B_e\left(1 - \frac{\alpha_e}{2B_e} + \ldots\right)$$

8.4 PARTITION FUNCTION FOR A DIATOMIC MOLECULE WITH COUPLED ROTATION-VIBRATION EFFECTS

The partition function for a vibrating diatomic rotator with energy levels given in equation (8.16) is the double sum

$$Q = \sum_v \sum_J (2J+1)\, e^{-u(v - xv^2) - J(J+1)\sigma[1 - \gamma J(J+1) - \delta v]} \tag{8.17}$$

where

$$u = \frac{\hbar\omega}{kT}, \qquad \sigma = \frac{B}{kT}, \qquad x = \frac{x\omega}{\omega}, \qquad \gamma = \frac{D}{B}, \qquad \delta = \frac{\alpha}{B}$$

The sum over J is approximated by the integral

$$\sum_J (2J+1) e^{-\sigma J(J+1)[1 - \gamma J(J+1) - \delta v]} \approx \int_0^\infty e^{-\sigma(1-\delta v)z + \gamma\sigma z^2}\, dz$$

$$\approx \int_0^\infty (1 + \gamma\sigma z^2) e^{-\sigma(1-\delta v)z}\, dz \tag{8.18}$$

The variable of integration $z = J(J+1)$. The $exp(\gamma\sigma z^2)$ can be expanded in the last expression in equation (8.18) because the product $\gamma\sigma$ is so small that higher-order terms are negligible. Let the variable $y = \sigma(1 - \delta v)z$; then the integral becomes, to terms of first order,

$$\int_0^\infty \left(1 + \frac{\gamma}{\sigma} y^2 + \ldots\right) e^{-y} \frac{dy}{\sigma(1-\delta v)} \approx \frac{1}{\sigma(1-\delta v)}\left(1 + \frac{2\gamma}{\sigma} + \ldots\right) = \frac{1}{\sigma}\left(1 + \frac{2\gamma}{\sigma} + \delta v + \ldots\right) \tag{8.19}$$

The partition function is now the sum

$$Q = \sum_{v=0}^{\infty} \frac{1}{\sigma}\left(1 + \frac{2\gamma}{\sigma} + \delta v\right)e^{-u(v-xv^2)} \tag{8.20}$$

Expand e^{uxv^2} to $1 + uxv^2$ and substitute in equation (8.20), to obtain

$$Q = \sum_{v=0}^{\infty} \frac{1}{\sigma}\left(1 + \frac{2\gamma}{\sigma} + \delta v + uxv^2 + \ldots\right)e^{-uv} \tag{8.21}$$

The sums involved are

$$\sum e^{-uv} = (1 - e^{-u})^{-1} \tag{8.22a}$$

$$\sum ve^{-uv} = -\frac{d}{du}\left(\sum e^{-uv}\right) = e^{-u}(1 - e^{-u})^{-2} \tag{8.22b}$$

$$\sum v^2e^{-uv} = -\frac{d}{du}\left(\sum ve^{-uv}\right) = (e^{-u} + e^{-2u})(1 - e^{-u})^{-3} \tag{8.22c}$$

and the partition function finally becomes

$$Q = \frac{1}{\sigma(1 - e^{-u})}\left[1 + \frac{2\gamma}{\sigma} + \frac{\delta}{e^{u} - 1} + \frac{2xu}{(e^{u} - 1)^2} + \ldots\right] \tag{8.23}$$

which may be expressed as the usual product of the separable vibrational and rotational partition functions and a correction term

$$Q = Q_vQ_r(1 + \Gamma T) \tag{8.24}$$

where the correction term is

$$1 + \Gamma T = 1 + \frac{2DkT}{B^2} + \frac{\alpha/B}{e^{\hbar\omega/kT} - 1} + \frac{2x\hbar\omega/kT}{(e^{\hbar\omega/kT} - 1)^2} \tag{8.25}$$

The correction becomes appreciable only at temperatures somewhat larger than $\hbar\omega/k$, and the coefficient Γ can be approximated as

$$\Gamma \simeq \frac{2Dk}{B^2} + \frac{\alpha k}{B\hbar\omega} + \frac{2xk}{\hbar\omega} \simeq \frac{8Bk}{\hbar^2\omega^2} + \frac{\alpha k}{B\hbar\omega} + \frac{2xk}{\hbar\omega} \tag{8.26}$$

The coefficient Γ has essentially the same value whether the factors B_e, D_e, ω_e, x_e, and α_e or the factors B_o, D_o, ω_o, x_o and α_o are used in equation (8.26).

In addition to the coupling that exists between vibrational and rotational energy, rather strong coupling usually exists between electronic energy and both vibrational and rotational energy. However, electronic states are typically widely spaced so that very few atoms and molecules exist in the excited electronic states at normal temperatures. In this case, it is a fair approximation to use the vibrational-rotational partition function for the ground state species as the partition function for all states. At higher temperatures, the coupling is accurately accounted for by treating each electronic state as a separate species, with its own characteristic values of B, D, ω, x, and α. Values for the higher electronic state are not always known, but a partial table of these coefficients is given by Herzberg (ref. 2), and an updated compilation is available in reference 14.

8.5 INTERMOLECULAR FORCES

Long-range attractive forces exist between molecules, even very inert molecules, which, at high density, perturb the energy levels and so modify the partition function. The existence of attractive intermolecular forces is strikingly demonstrated by the fact that liquids exist, and by the Joule-Thomson effect in which adiabatically expanding gases are cooled in accordance with the work done against these forces. In preparation for modeling the phenomena of intermolecular attraction, consider first the interaction of atoms and molecules in the presence of a fixed external electric field ε.

Generally, molecules may be unsymmetrical and possess a permanent dipole moment d resulting from the unsymmetrical distribution of the electron charge. Usually, the asymmetry is confined to one or two electrons in the outer shell. It is common practice to treat the dipole as though it were the result of a single-electron charge with a displacement x from the center of mass, which is the center of residual positive charge. In other words, a distance x is defined so that $d = ex$.

The interaction energy between the field ε and a permanent dipole moment d is

$$U = -\vec{\varepsilon} \cdot \vec{d} = -\varepsilon d \cos \theta \tag{8.27}$$

where θ is the angle between the dipole vector and the field. Strictly speaking, the orientations are quantized, of course, but molecules generally have large enough moments of inertia that a continuous classical variation in θ is adequate.

If the orientations were completely random so that all values of θ were equally probable, the average dipole moment would be zero. However, the dipoles take a Boltzmann distribution in which the tendency for the dipoles to line up in the minimum energy configuration ($\theta = 0$) is counteracted by the thermal energy of rotation. Where the dipole energy U is very small compared to kT, the fraction of molecules with a given orientation θ is approximately

$$f(\theta)d\theta \approx \frac{1}{2} e^{(\varepsilon d \cos\theta)/kT} \sin\theta \, d\theta \tag{8.28}$$

The average dipole moment in the direction of the field is then

$$\bar{d} \approx \frac{1}{2} \int_0^\pi d \cos\theta \left(1 + \frac{\varepsilon d \cos\theta}{kT}\right) \sin\theta \, d\theta = \frac{\varepsilon d^2}{3kT} \tag{8.29}$$

and the average interaction energy is

$$\bar{U} = -\varepsilon\bar{d} \approx -\frac{\varepsilon^2 d^2}{3kT} \tag{8.30}$$

At very low temperatures or in very strong fields, the average dipole approaches d as an upper limit, since the dipoles all line up in the field direction, and the interaction energy then approaches εd.

Problem 8.1: Show that the normalized Boltzmann distribution for a collection of classical dipoles in a fixed electric field ε is

$$f(\theta)d\theta = \frac{e^{(\varepsilon d \cos\theta)/kT} \sin\theta \, d\theta}{\frac{kT}{\varepsilon d}\left(e^{\varepsilon d/kT} - e^{-\varepsilon d/kT}\right)} \tag{8.28a}$$

and that the average dipole moment is

$$\bar{d} = d\left(\coth\frac{\varepsilon d}{kT} - \frac{kT}{\varepsilon d}\right) \tag{8.29a}$$

$$\bar{d} \xrightarrow[\frac{\varepsilon d}{kT} \gg 1]{} d$$

$$\bar{d} \xrightarrow[\frac{\varepsilon d}{kT} \ll 1]{} \varepsilon d^2/3kT$$

Atoms and symmetrical molecules do not have a permanent dipole, but the external field distorts the electron distribution and induces a dipole that interacts with the field. This effect also occurs in molecules with a permanent dipole and should be added to the effect considered above. Normally, the external field is small compared with the strength of the nuclear field in which the electron moves, so the shift in electron density from the nuclear center in the direction of the field is small. There is a close analogy between this situation and the orientation of dipoles except that, in place of the thermal energy of rotation that opposes the orientation of the dipoles, the kinetic energy of electronic motion opposes any displacement of the electronic charge away from the nucleus. A rigorous analysis of the perturbations of energy levels produced by an external electric field (the Stark effect) is described by Bethe and Salpeter (ref. 3) for one- and two-electron atoms; numerical methods are required for more complicated atoms and molecules. For present purposes, we are interested mainly in the functional relationships between the interaction energy and internuclear distance rather than quantitatively accurate values, and we shall treat the electronic charge as though it were a dipole of moment ea oscillating about the nuclear center with a kinetic energy equal to the ionization energy I. By analogy with equation (8.29), the average dipole in the direction of the field, that is, $\alpha\varepsilon$, can be expressed approximately as

$$\bar{d} = \alpha\varepsilon \approx \frac{e^2a^2}{3I}\,\varepsilon \qquad (8.31)$$

In the absence of other information, the order of magnitude of the distance a can be taken as the Bohr radius $\hbar^2/\mu e^2$. Better yet, ea can be estimated from the polarizability α, which is related to a measured dielectric constant η (ref. 4),

$$\eta = 1 + \frac{4\pi N\bar{d}}{\varepsilon} = 1 + 4\pi N\alpha + \frac{4\pi Nd^2}{3kT} \qquad (8.32)$$

where N is the number density of the gas. A plot of $(\eta - 1)$ versus T^{-1} is a linear relation with slope $4\pi Nd^2/3k$ and the extrapolated intercept at infinite temperature $4\pi N\alpha$. More precise methods are available for measuring the permanent dipole moment d by use of a high-frequency electromagnetic wave to precess the dipoles about an imposed electric field; the resonance frequency of precession is related to the value of d. Then α may be determined from a single measurement of η at normal temperature.

The interaction energy of the polarizable molecule with an imposed field is

$$U = -\varepsilon\bar{d} \sim -\varepsilon^2\,\frac{e^2a^2}{3I} \qquad (8.33)$$

With the energies of interaction between molecules and a fixed electric field in mind, next consider interactions between the molecules themselves. First, the interactions that involve ions are summarized, then the interactions involving permanent dipoles and, finally, interactions involving neutral gas particles.

Ion-Ion Interactions

In this case, the interaction is simply that of the charge of one ion, Z_1e, in the Coulomb potential of the other ion, Z_2e/r:

$$U = \frac{Z_1Z_2e^2}{r} \qquad (8.34)$$

and the interaction energy is proportional to r^{-1}. There is no orientation effect. Polarizability effects also occur, but these are normally much smaller than the Coulomb interaction and can be disregarded.

Ion-Dipole Interactions

At normal temperatures, the interaction energy is the energy of the average dipole $\bar{d}$ in the Coulomb field of the ion:

$$U = -\frac{Ze}{r^2}\bar{d} = -\frac{Z^2e^2}{r^4}\frac{d^2}{3kT} \tag{8.35}$$

The interaction energy varies as r^{-4} in this case. At very low temperatures, $\bar{d}$ approaches its limiting value of d; then the interaction varies as r^{-2}.

Ion-Polarization Interaction

The field of the ion induces a dipole $\alpha Ze/r^2$ in a neutral gas particle, and the interaction energy again varies as r^{-4}:

$$U = -\frac{Zed}{r^2} = -\alpha\frac{Z^2e^2}{r^4} \tag{8.36}$$

but, in this case, independent of temperature since there is no orientation effect.

Dipole-Dipole Interaction

The electric field surrounding the dipole d_1 has the magnitude (ref. 4)

$$\epsilon = \frac{d_1}{r^3}(1 + 3\cos^2\theta)^{1/2} \tag{8.37}$$

where θ is the angle between d_1 and the radius vector $\vec{r}$ between the two dipoles. The average dipole of d_2 in the direction of this field is $\epsilon d_2{}^2/3kT$, and the interaction energy is

$$U = -\epsilon\bar{d}_2 = -\frac{\epsilon^2 d_2{}^2}{3kT} = -\frac{d_1{}^2d_2{}^2}{3kTr^6}(1 + 3\cos^2\theta) \tag{8.38}$$

The dipole interactions are normally small compared with kT, so the average value of $\cos^2\theta$ over all 4π steradian of the solid angle is approximately 1/3 and

$$\bar{U} \approx -\frac{2d_1{}^2d_2{}^2}{3kTr^6} \tag{8.39}$$

Thus, even though dipole-dipole energy decreases as r^{-3} in strong fields, the average decreases much more rapidly in weak fields, namely, as r^{-6} because of thermal randomization of the dipoles.

Dipole-Polarization Interaction

The field of the dipole, equation (8.37), induces the dipole $\alpha\epsilon$ in the direction of the field and leads to an interaction energy again proportional to r^{-6}:

$$\bar{U} = -\alpha\epsilon^2 = -\frac{\alpha d^2}{r^6}\,\overline{(1 + 3\cos^2\theta)} = -\frac{2\alpha d^2}{r^6} \tag{8.40}$$

which is relatively independent of temperature under normal conditions.

Polarization-Polarization Interaction

The interaction between two neutral particles is the most common collision interaction in gases at normal temperatures. In this case, the outer electrons moving relative to the center of charge behave as oscillating dipoles and induce the similarly oscillating dipoles of neighboring gas particles to move in the same phase. Thus two interacting particles behave as a pair of coupled oscillators.

The analogy between interacting neutral molecules and a pair of coupled oscillators was developed by London (ref. 1) and, although the treatment of electronic motion as a harmonic oscillator yields only fair quantitative accuracy, the model is very helpful heuristically. Consider first the motion along a line between the centers of molecules (fig. 8.3). Let r be the distance between centers and x_1 and x_2, the displacements of negative charge from the nuclei at any instant of time. The interaction potential is thus

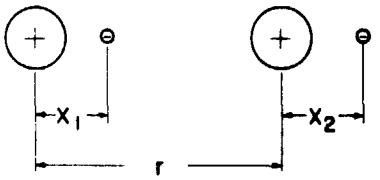

Figure 8.3.- Coordinate system for colinear pair of one-dimensional oscillating dipoles.

$$V = e^2\left(\frac{1}{r} + \frac{1}{r + x_2 - x_1} - \frac{1}{r - x_1} - \frac{1}{r + x_2}\right)$$
$$\approx -\frac{2e^2 x_1 x_2}{r^3} \tag{8.41a}$$

Then the Schroedinger equation for the system of two equivalent oscillators is

$$\frac{\partial^2\psi}{\partial x_1^2} + \frac{\partial^2\psi}{\partial x_2^2} + \frac{2\mu}{\hbar^2}\left(E_1 + E_2 - \frac{\mu\omega^2 x_1{}^2}{2} - \frac{\mu\omega^2 x_2{}^2}{2} + \frac{2e^2 x_1 x_2}{r^3}\right)\psi = 0 \tag{8.42a}$$

where $\hbar\omega/2$ is the energy of the unperturbed oscillators in their ground state, approximately the ionization energy I. Separation of variables is effected by the transformation

$$x_1 = \frac{z_1 + z_2}{\sqrt{2}} \tag{8.43a}$$

$$x_2 = \frac{z_1 - z_2}{\sqrt{2}} \qquad (8.43b)$$

$$x_1 x_2 = \frac{z_1{}^2 - z_2{}^2}{2} \qquad (8.43c)$$

and the Schroedinger equation then becomes

$$\frac{\partial^2\psi}{\partial z_1{}^2} + \frac{\partial^2\psi}{\partial z_2{}^2} + \frac{2\mu}{\hbar^2}\left[E_1 + E_2 - \frac{\mu z_1{}^2}{2}\left(\omega^2 - \frac{2e^2}{\mu r^3}\right) - \frac{\mu z_2{}^2}{2}\left(\omega^2 + \frac{2e^2}{\mu r^3}\right)\right]\psi = 0 \qquad (8.42b)$$

The separable wave function $\psi = \psi_1(z_1)\psi_2(z_2)$ is a solution to equation (8.42b). The ground state energies of these uncoupled oscillators are

$$E_1 = \frac{\hbar}{2}\left(\omega^2 - \frac{2e^2}{\mu r^3}\right)^{1/2} \qquad (8.44a)$$

$$E_2 = \frac{\hbar}{2}\left(\omega^2 + \frac{2e^2}{\mu r^3}\right)^{1/2} \qquad (8.44b)$$

The total energy of the system is

$$E_1 + E_2 = \frac{\hbar\omega}{2}\left[\left(1 - \frac{2e^2}{\mu\omega^2 r^3}\right)^{1/2} + \left(1 + \frac{2e^2}{\mu\omega^2 r^3}\right)^{1/2}\right] \approx \hbar\omega\left(1 - \frac{e^4}{2\mu^2\omega^4 r^6} + \cdots\right) \qquad (8.44c)$$

The first term in equation (8.44c) is just the energy of the two unperturbed oscillators, so the interaction energy is the second term

$$U \approx -\left(\frac{e^4}{2\mu^2\omega^4 r^6}\right)\hbar\omega \qquad (8.45a)$$

One might relate the total oscillator energy $\hbar\omega/2$ and $(1/2)\mu\omega^2 a^2$ to the ionization energy I or to the polarizability α given in equation (8.31) to demonstrate the functional relationships between these quantities

$$U \sim -\frac{e^4 a^4}{4Ir^6} \sim -\frac{9}{4}\,\frac{\alpha^2 I}{r^6} \qquad (8.46)$$

However, the harmonic oscillator analogy should not be pushed too far quantitatively; the numerical coefficients given can only be expected to give order-of-magnitude accuracy. The principle point is that the interaction energy between neutral particles is predicted to vary as r^{-6}.

Problem 8.2: Show that the interaction potential for dipole oscillators that vibrate normal to the line between centers is approximately

$$V = \frac{e^2 y_1 y_2}{r^3} \tag{8.41b}$$

and that the interaction energy for coupled oscillators in such modes of vibration is

$$U = -\left(\frac{e^4}{8\mu^2\omega^4 r^6}\right)\hbar\omega \tag{8.45b}$$

The total interaction energy for three independent modes of oscillation, one parallel and two normal to the radius vector between particles, would thus be 3/2 larger than given in equation (8.45a).

Other types of molecular forces occur, of course. Some molecules, such as CO_2, have no dipole moment but possess strong quadrupoles. However, dipole-quadrupole and quadrupole-quadrupole interactions decrease as r^{-8} and r^{-10}, respectively, and normally have a much shorter range than the interactions considered above. Usually, these are ignored because the very strong repulsive forces begin to take over at these short ranges anyway. Qualitatively, the repulsive forces are associated with the potential of charge distributions. For example, the potential of a charge distribution $\psi^2(r')$ at point r may be expressed as

$$U(r) = \int \frac{\psi^2(r')}{r' - r}\, d\tau' \tag{8.47a}$$

This potential is weighted so heavily at the point r that, to a first approximation, the potential is proportional to the charge density at that point:

$$U(r) \sim \psi^2(r) \sim e^{-2r/a} \tag{8.47b}$$

Since the wave functions all decrease exponentially, one expects the interaction potential to decrease exponentially as indicated in equation (8.47b). Unfortunately, exponential forms are sometimes difficult to treat in analytic problems, and a simple inverse-power relation is often easier to handle:

$$U(r) \sim \frac{U_o}{r^n} \tag{8.47c}$$

If the exponent n is taken to be 12, the behavior is something like an exponential repulsion over a reasonable range of energy. A still simpler approximation often useful is to let the repulsive potential be a discontinuous jump to $+\infty$ at some distance r_o where the repulsive potential balances the attractive potentials considered above. A combined hard sphere and attractive potential of the form

$$\left.\begin{aligned} U(r) &= \infty & r &< r_o \\ &= \frac{U_o}{r^n} & r_o &< r \end{aligned}\right\} \tag{8.48}$$

is found to be reasonably realistic for some calculations where the coefficient n is taken to be 6 for neutral particle interactions and 4 for ion-neutral particle interactions (as discussed above). The coefficient γ_0 is a constant or is proportional to $(kT)^{-1}$, depending on whether the molecules have zero or finite permanent dipole moment.

8.6 PARTITION FUNCTION WITH DISPERSION FORCES

The long-range attractive forces discussed in section 8.5 are known as dispersion forces. We now consider the general form of the partition function when gas molecules move in the presence of such forces.

The total Hamiltonian for a system of N identical particles with mass m is

$$H(p,q) = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + U(q_1, q_2, \ldots, q_{3N}) \tag{8.49}$$

where the $3N$ coordinates q_i are conjugate to the momenta coordinates p_i. In contrast to earlier chapters, N does not necessarily mean the Avagadro number here. The total partition function for the entire system of N particles, expressed in terms of the classical phase integral, is

$$\begin{aligned} Q_N &= \frac{1}{N!h^{3N}} \int \cdots \int e^{-H(p_i,q_i)/kT}\, dp_1\, dp_2 \ldots dq_{3N} \\ &= \frac{1}{N!} \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} \int \cdots \int e^{-U(q_i)/kT}\, dq_1 \ldots dq_{3N} \end{aligned} \tag{8.50}$$

The factor $N!$ in the denominator is required to account for the number of ways identical particles can be interchanged without altering the system. The remaining integral over the coordinates is called the configuration integral, I. Note that if the interaction energy U is everywhere zero, the configuration integral becomes V^N, where V is the total volume of the system. In this case,

$$Q_N \xrightarrow[U \to 0]{} \frac{Q^N}{N!} \tag{8.51}$$

where Q is the usual single-particle partition function obtained previously for very dilute gases, that is, where gas particles are so far from all neighbors on the average that the interaction potentials can be neglected. If $U(q_i)$ is nonvanishing over a very small percentage of the space, then the configuration integral is expected to be almost the Nth power of volume, approximately $V^N(1 - \varepsilon)^N$ or $V^N(1 - N\varepsilon + \ldots)$, where ε is a small quantity and $\varepsilon < 0$ if $U < 0$. Note that the internal degrees of freedom of the molecules are all treated as independent here; the q_i terms in the configuration integral are external or position coordinates of the molecules only.

Problem 8.3: Show that if the system contains a mixture of gases with N_1 identical particles of mass m_1, N_2 identical particles of mass m_2, etc., the partition function for the total system of $N = (N_1 + N_2 + \ldots)$ particles becomes

$$Q_N = \frac{1}{N_1!}\left(\frac{2\pi m_1 kT}{h^2}\right)^{3N_1/2} \cdot \frac{1}{N_2!}\left(\frac{2\pi m_2 kT}{h^2}\right)^{3N_2/2} \cdot\cdot\cdot \iint e^{-U(q_i)/kT}\, dq_1 \ldots dq_{3N} \tag{8.50a}$$

and that in the limit as U vanishes everywhere:

$$Q_N \to \frac{Q_1^{N_1}}{N_1!} \cdot \frac{Q_2^{N_2}}{N_2!} \ldots V^N \tag{8.51a}$$

Assume now that the potential is the sum of all pair potentials

$$U(q_i) = \sum_{i,j \neq i} U(r_{ij}) \tag{8.52}$$

This is not strictly true, but it is a useful approximation. The configuration integral I may then be expressed as

$$I = \int \ldots \int e^{-\sum_{i,j} U(r_{ij})/kT}\, dx_1\, dy_1\, dz_1 \ldots dx_N\, dy_N\, dz_N \tag{8.53}$$

Consider first the integral over the coordinates of the first molecule, x_1, y_1, and z_1, which interacts with $N-1$ other molecules:

$$\iiint e^{-\sum_{i\neq 1} U(r_{i1})/kT}\, dx_1\, dy_1\, dz_1 = \iiint \prod_{i\neq 1} \left\{1 + \left[e^{-U(r_{i1})/kT} - 1\right]\right\} dx_1\, dy_1\, dz_1$$

$$= \iiint \left\{1 + \sum_{i\neq 1}\left[e^{-U(r_{i1})/kT} - 1\right] + \ldots\right\} dx_1\, dy_1\, dz_1 \tag{8.54}$$

If $U(r_{i1})/kT$ is always very small compared with unity, we can neglect all but the first-order terms and express the integral in equation (8.54) as

$$V + \iiint \sum_{i\neq 1}\left[e^{-U(r_{i1})/kT} - 1\right] dx_1\, dy_1\, dz_1 = V + (N-1)\beta \tag{8.55}$$

where β is defined, using either Cartesian or polar coordinates, as

$$\beta = \iiint \left[e^{-U(r)/kT} - 1\right] dx\, dy\, dz = 4\pi \int_0^\infty \left[e^{-U(r)/kT} - 1\right] r^2\, dr \tag{8.56}$$

Follow the same procedure for the second molecule, noting that the interaction with the first molecule has already been included so that the interactions with $N-2$ other molecules remain to be included, then for the third molecule $N-3$ interactions remain, and so on. The configuration integral thus becomes

$$\begin{aligned} I &= V^N\left(1 + \frac{N-1}{V}\beta\right)\left(1 + \frac{N-2}{V}\beta\right)\left(1 + \frac{N-3}{V}\beta\right) \cdot \cdot \cdot 1 \\ &= V^N\left\{1 + [(N-1) + (N-2) + (N-3) + \cdot \cdot \cdot + 1]\frac{\beta}{V} + O\left(\frac{\beta}{V}\right)^2 + \cdot \cdot \cdot\right\} \\ &= V^N\left[1 + \frac{N(N-1)}{2}\frac{\beta}{V} + O\left(\frac{\beta}{V}\right)^2 + \cdot \cdot \cdot\right] \\ &\approx V^N\left(1 + \frac{N}{2}\frac{\beta}{V}\right)^N \end{aligned} \tag{8.57}$$

The logarithm of the configuration integral is approximately

$$\ln I = N \ln V + \frac{N^2\beta}{2V} + \cdot \cdot \cdot \tag{8.58}$$

and the logarithm of the total partition function of the system is

$$\ln Q_N = N \ln \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V + \frac{N^2\beta}{2V} - \ln N! \tag{8.59}$$

The thermodynamic properties of gases are usually expressed in terms of the single-particle partition function Q, which is related to Q_N through equation (8.51) by

$$\ln Q = \frac{1}{N}(\ln Q_N + \ln N!) = \ln \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V + \frac{N\beta}{2V} \tag{8.60}$$

The first term is just the free-particle translational partition function and the second term is the correction for dispersion forces, which vanishes as the gas becomes infinitely dilute, $(N/V) \to 0$.

The pressure of a gas with dispersion forces is thus

$$P = RT\frac{\partial \ln Q}{\partial V} = \frac{RT}{V}\left(1 - \frac{N\beta}{2V} + \cdot \cdot \cdot\right) \tag{8.61a}$$

Compare this with the virial equation of state:

$$P = \frac{RT}{V}\left(1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + . . .\right) \tag{8.61b}$$

An expression for the first virial coefficient in terms of the dispersion potential is thus

$$B(T) = -\frac{N\beta}{2} = -2\pi N\int_0^\infty \left[e^{-U(r)/kT} - 1\right]r^2\,dr \tag{8.62}$$

At very low temperatures, the region where the interaction potential is negative, $U(r) < 0$, contributes most to the integral β and the correction coefficient $B(T)/V$ is then negative. At very high temperatures, the inner core region where the interaction potential is large and positive contributes most to the integral β and $B(T)/V$ then becomes positive. The temperature where the coefficient $B(T)$ vanishes is known as the Boyle temperature; Boyle's law of gases is valid over a wide range of pressures near this temperature. Typical Boyle temperatures range from 18° K for He and 100° K for H_2 to 325° K for N_2, 422° K for O_2, and 426° K for Ar. For temperatures much larger than the Boyle temperature, the integral $(-\beta)$ approaches a constant that represents the volume where the potential is essentially impenetrable. For most molecules, this volume is the order of 6×10^{-23} cm^3, corresponding to the range of ground state wave functions that have a radial extent of about 1.3×10^{-8} cm. Thus a limiting upper value of $B(T)$ is about 20 cm^3. Divided by the molar volume of the gas considered, this value gives the magnitude of the correction at temperatures well above the Boyle temperature; for example, at normal densities, $V = 22{,}400$ cm^3 and $(B/V) \approx 10^{-3}$. The negative corrections below the Boyle temperature depend on the long-range attractive potential function and are not so simply characterized as the limit above, but they are typically the same order of magnitude. For example, at standard temperature and pressure, $(-B/V)$ is about 10^{-3} for O_2 and N_2. At lower densities, the corrections are proportionately smaller.

8.7 FREE ENERGY AND FUGACITY

The chemist describes deviations from ideal gas behavior in terms of the fugacity, f (refs. 5 and 6). This quantity may be defined in terms of the Gibbs free energy G as

$$G - G^o = RT\,ln\,\frac{f}{f^o} \tag{8.63}$$

where G^o and f^o are the free energy and fugacity at some standard state. Normally, the standard free energy is taken to be at such low pressure that G^o is the ideal gas value and the standard fugacity f^o is the pressure.

Neglect the coupling between internal and external degrees of freedom so that the partition function may be expressed as the product of translational and internal energy partition functions:

$$Q \simeq Q_t Q_{int} \tag{8.64}$$

Then, if one allows for dispersion force corrections, the Gibbs free energy becomes

$$\begin{aligned} G &= -RT\left(ln\,\frac{Q}{N} + 1\right) + PV \\ &= -RT\left[ln\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{V}{N} + \frac{N\beta}{2V} + ln\,Q_i + 1\right] + PV \end{aligned} \tag{8.64a}$$

The standard state at very low pressure where $N\beta/V = 0$ and $PV = RT$ becomes

$$G^o = -RT\left[ln\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{V^o}{N} + ln\,Q_i\right] \tag{8.64b}$$

so the difference in free energy is

$$G - G^o = -RT\left(1 + ln\,\frac{V}{V^o} + \frac{N\beta}{2V}\right) + PV \tag{8.65}$$

If equation (8.65) is compared with (8.63), the fugacity ratio may be expressed as

$$\begin{aligned} ln\,\frac{f}{f^o} &= \frac{PV}{RT} - \left(1 + ln\,\frac{V}{V^o} + \frac{N\beta}{2V}\right) \\ &= \left(1 - \frac{N\beta}{2V} + \ldots\right) - \left(1 + ln\,\frac{V}{V^o} + \frac{N\beta}{2V}\right) \\ &= -ln\,\frac{V}{V^o} - \frac{N\beta}{V} + \ldots \end{aligned} \tag{8.66a}$$

Since the standard fugacity $f^o = p^o = RT/V^o$,

$$ln\,f = ln\,\frac{RT}{V} - \frac{N\beta}{V} + \ldots \tag{8.66b}$$

The ratio $N\beta/V$ is very small compared with unity and the fugacity is approximately

$$f \approx \frac{RT}{V}\left(1 - \frac{N\beta}{V}\right)$$

$$\approx p\left(1 + \frac{N\beta}{2V} + \ . \ . \ .\right)\left(1 - \frac{N\beta}{V}\right)$$

$$\approx p\left(1 - \frac{N\beta}{2V} + \ . \ . \ .\right) \approx p\left[1 + \frac{B(T)}{V}\right] \tag{8.66c}$$

8.8 THE VAN DER WAALS GAS

The van der Waals gas is an approximation obtained when the potential function is taken to be a combination of hard sphere and long-range attractive potentials:

$$\left.\begin{aligned} U(r) &= \infty \quad , \qquad r < r_o \\ &= U(r) \ , \qquad r > r_o \end{aligned}\right\} \tag{8.67}$$

The integral β is then

$$\beta = -4\pi\int_c^{r_o} r^2 \, dr + 4\pi \int_{r_o}^{\infty} \left[e^{-U(r)/kT} - 1\right] r^2 \, dr$$

$$\approx -\frac{4\pi r_o^{\,3}}{3} - \frac{4\pi}{kT}\int_{r_o}^{\infty} U(r) r^2 \, dr \tag{8.68}$$

The first virial coefficient $B(T)$ may be expressed as

$$B(T) = -\frac{N\beta}{2} = \frac{2N\pi r_o^{\,3}}{3} + \frac{2\pi N^2}{RT}\int_{r_o}^{\infty} U(r) r^2 \, dr$$

$$= b - \frac{a}{RT} \tag{8.69}$$

The quantity b is one-half the volume preempted by the hard sphere part of the potential. The quantity a is positive when $U(r)$ is negative, and thus is a measure of the magnitude of the attractive potential. The equation of state may now be expressed as

$$PV = RT\left[1 + \frac{1}{V}\left(b - \frac{a}{RT}\right)\right] \tag{8.70}$$

which is the same as the empirical van der Waal equation:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$PV = RT + b\left(P + \frac{a}{V^2}\right) - \frac{a}{V}$$

$$\simeq RT\left[1 + \frac{b}{V\left(1 - \frac{b}{V}\right)} - \frac{a}{VRT}\right] \tag{8.70a}$$

except for a factor [1 - (b/V)] in the denominator of the second term, which can be replaced by unity for reasonably dilute gases. The van der Waal equation may be expected to remain valid so long as virial coefficients beyond the first can be safely ignored.

For induced-dipole, induced-dipole type interactions between neutral particles, an expression for a may be developed from the interaction potential in equation (8.46):

$$a = -2\pi N^2 \int_{r_o}^{\infty} U(r) r^2 \, dr \simeq \frac{9}{2}\pi N^2 \alpha^2 I \int_{r_o}^{\infty} \frac{dr}{r^4} = \frac{3\pi N^2 \alpha^2 I}{2 r_o^3} \tag{8.71}$$

8.9 EQUATION OF STATE NEAR THE CRITICAL POINT

Most of the discussions here have had the purely gas phase in mind, but at very low temperatures and high pressures, mixtures of liquid and vapor phase occur and the ideal gas relations must be severely modified. The critical temperature T_c is defined as that temperature above which no liquid phase can be formed at any pressure. The critical pressure p_c is the pressure at which the gas phase just maintains equilibrium with the liquid at the critical temperature, and the critical volume V_c is the volume of a fixed mass of gas at p_c and T_c. The equation of state near the critical point can be approximated reasonably well with the van der Waal equation, but the value of R need not be the gas constant. A reduced form of the van der Waal equation is the most satisfactory approximation, obtained by dividing equation (8.70a) by the product $p_c V_c$:

$$\frac{1}{p_c V_c}\left(p + \frac{a}{V^2}\right)(V - b) = \left[\frac{p}{p_c} + \frac{\frac{a}{p_c V_c^2}}{\left(\frac{V}{V_c}\right)^2}\right]\left(\frac{V}{V_c} - \frac{b}{V_c}\right) = \frac{RT_c}{p_c V_c}\left(\frac{T}{T_c}\right) \tag{8.72}$$

$$\left(p^* + \frac{a^*}{V^{*2}}\right)(V^* - b^*) = R^* T^* \tag{8.72a}$$

where p^*, V^*, and T^* are the pressure, volume, and temperature, respectively, in units of the critical values p_c, V_c, and T_c. The equation must be satisfied at the critical point ($p^* = V^* = T^* = 1$) and have an inflection at that point, which requires that

$$a^* = \frac{a}{p_c V_c^2} = 3 \tag{8.73a}$$

$$b^* = \frac{b}{V_c} = \frac{1}{3} \tag{8.73b}$$

$$R^* = \frac{RT_c}{p_c V_c} = \frac{8}{3} \tag{8.73c}$$

Note that R^* would be unity for an ideal gas. The reduced form of the van der Waal equation then becomes

$$\left(p^* + \frac{3}{V^{*2}}\right)(3V^* - 1) = 8T^* \tag{8.74}$$

This equation is found to reproduce reasonably well the behavior of most compounds in the liquid phase and in the vapor phase near the critical point. However, in the mixed liquid-vapor phase, the phase fractions change in such a way that the pressure remains constant (the vapor pressure at the given temperature) over a wide range of specific volume, whereas p^* is a cubic function of V^* over this range according to equation (8.74). The domain of mixed phase may be estimated from an empirical relation for vapor pressure found by van der Waals (ref. 5);

$$p_v^* = e^{-C[(1/T^*)-1]} \tag{8.75}$$

where C is a characteristic constant of the vapor (e.g., about 5.52 for O_2 and 5.62 for N_2). The boundaries of the mixed-phase region on a p^*V^* plot occur where the vapor pressure in equation (8.75) intersects the isotherms given in equation (8.74). Figure 8.4 shows the isotherms for N_2 with $C = 5.62$. An approximate solution to equation (8.74) at the vapor boundary where $V^* >> 1$, which also satisfies conditions at the critical point, is

$$V_v^* \approx \frac{8T^*}{3p^*} - \frac{5}{3} \tag{8.76}$$

The empirical constant C can be related to the heat of vaporization ΔH through the Clausius-Clapeyron equation

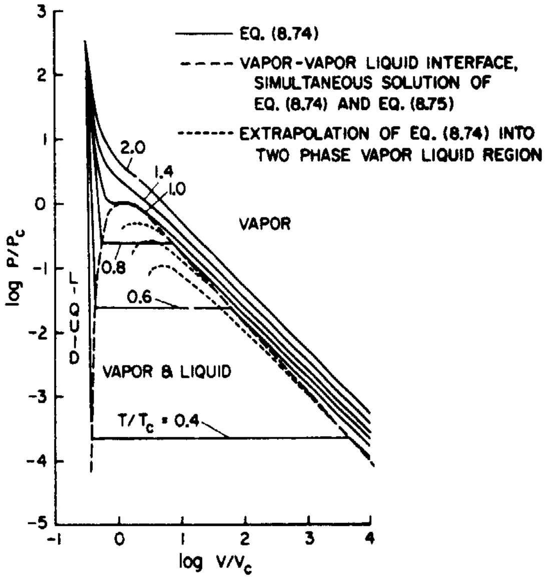

Figure 8.4.- Equation of state near critical point for gas with vapor pressure given by $p_v/p_c = exp[5.62(1 - T_c/T)]$.

(refs. 5 and 6)

$$\frac{dp_v}{dT} = \frac{\Delta H}{T\ \Delta V} \tag{8.77a}$$

In reduced form, this equation becomes

$$\frac{dp_v^*}{dT^*} = \left(\frac{\Delta H}{p_c V_c}\right)\frac{1}{T^*\ \Delta V^*} \tag{8.77b}$$

Near the liquid boundary, the liquid volume is approximately the critical volume, and the change in volume V^* is, from equation (8.76), approximately

$$\Delta V^* = V_v^* - V_l^* \simeq \frac{8T^*}{3p^*} - \frac{8}{3} \tag{8.78}$$

Then, from equations (8.75) and (8.77b),

$$\left(\frac{\Delta H}{p_c V_c}\right) = \frac{C p^*\ \Delta V^*}{T^*} \simeq \frac{8C}{3}\left(1 - \frac{p^*}{T^*}\right) \tag{8.79}$$

Equation (8.79) predicts a vanishing value for ΔH at the critical point and a constant value $(8C/3)(p_c V_c)$ far removed from the critical point. The constant C may be adjusted to agree with the observed ΔH at the boiling point (p_v = 1 atm), and the results will then be reasonably accurate elsewhere.

At first glance, it might appear that the equation of state near the critical point derived above does not depend in any way on the partition function. However, it is indeed related to the partition function; recall that equation (8.74) is derived from the van der Waal equation, and the latter can be derived directly from the partition function, with suitable approximations for the configuration integral.

Problem 8.4: Show that the values $a^* = 3$, $b^* = 1/3$, and $RT_c/P_cV_c = (1 + a^*)(1 - b^*)$ in the reduced form of van der Waal's equation

$$\left(p^* + \frac{a^*}{V^{*2}}\right)(V^* - b^*) = \left(\frac{RT_c}{p_c V_c}\right)T^*$$

satisfy conditions at the critical point and create an inflection point there.

8.10 CORRECTIONS TO ELECTRONIC PARTITION FUNCTIONS

As mentioned in chapter 7, the electronic energy states near the ionization limit become hydrogen-like for all atoms and molecules, and the partition function would become infinite (eq. (7.73)) if these levels were not effectively truncated. The truncation occurs because neighboring gas particles perturb the energy levels and, in effect, lower the ionization energy needed for the excited electron to escape from its parent nucleus. Although theories of the reduced ionization potential are far from precise, the actual value of the partition function is rather insensitive to the exact truncation point except at very high temperature, so the approximate theories are adequate for many conditions of interest.

Consider first a neutral gas of N randomly distributed particles in a volume N/ρ, where ρ is the number density. The probability that none of the N particles falls within a radius r about a test molecule is

$$P = \left(1 - \frac{\frac{4}{3}\pi r^3}{\frac{N}{\rho}}\right)^N \xrightarrow[N\to\infty]{} e^{-(4/3)\pi\rho r^3} \tag{8.80}$$

The average value of r is approximately

$$\bar{r} \simeq \langle r^3\rangle^{1/3} = \left(\frac{3}{4\pi\rho}\right)^{1/3} \tag{8.81}$$

and the maximum quantum number of the hydrogen-like orbit that falls within this radius is

$$n_m = \left(\frac{\bar{r}}{a_o}\right)^{1/2} \simeq \left(\frac{3}{4\pi\rho a_o{}^3}\right)^{1/6} \tag{8.82}$$

where a_o is the usual Bohr orbit.

To a first approximation, the partition function may simply be terminated at n_m, resulting in a finite limit weakly dependent on number density. A more rigorous approach would be to solve the Schroedinger equation for the perturbed energy levels, but this is rarely worth bothering with at the usual temperatures where neutral gases exist since the partition function is insensitive to the exact cut off chosen at these temperatures. At higher temperatures, the gas becomes ionized and the much stronger perturbations created by the positive ions and electron collisions become dominant.

Several theories for the effect of ion perturbations on weakly bound electronic states have been developed, but precise experimental validation of any of them has been lacking. Nevertheless, the various theories do give somewhat similar results and illustrate some of the mechanisms by which such perturbations must truncate the partition function. Perhaps the simplest theory and therefore a heuristically attractive one is that of Unsöld (ref. 7). This theory assumes that the perturbation is furnished solely by the nearest neighbor. The escape energy of a bound electron is reduced by the perturbation of a nearby ion (fig. 8.5). The Coulomb potential of the perturbing ion, with charge Z_1e , is added to the Coulomb potential of the central charge Ze. The distance between the ion and the perturbed particle is r, the distance from the center of the particle to the maximum potential is defined as b. Z is the effective screened change for the perturbed particle, approximately unity for a neutral atom, two for a single ionized atom, etc. The potential energy at this maximum is thus

$$V_m = -\frac{Ze^2}{b} - \frac{Z_1e^2}{r-b} \tag{8.83}$$

The effective potential change of the excited electron at the series limit is obtained by subtracting the average potential change due to the perturbing ion, that is, $-Z_1e^2/r$, from the maximum in the potential $-V_m$, given above. This change is related to the maximum quantum number n_m for the bound electron by

$$\Delta E = \frac{e^2Z^2}{2a_on_m^2} = e^2\left(\frac{Z}{b} + \frac{Z_1}{r-b} - \frac{Z_1}{r}\right)$$

$$= \frac{e^2}{r}\left[Z\left(1 + \frac{r-b}{b}\right) + Z_1\,\frac{b}{r-b}\right] \tag{8.84}$$

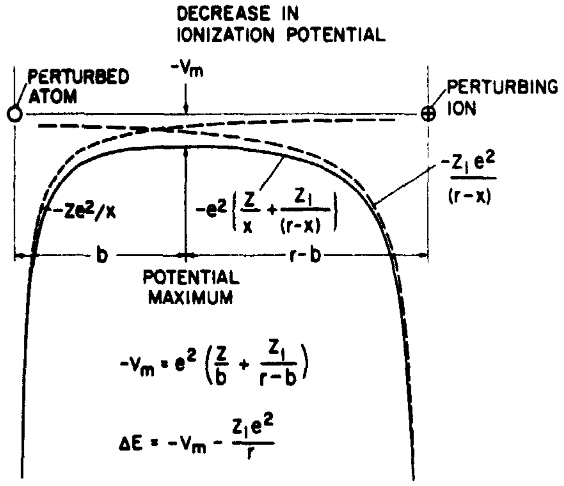

Figure 8.5.- Potential for electron bound to screened charge +Ze when perturbed by ion charge $+Z_1e$ at the distance r.

The ratio $(r-b)/b$ can be eliminated with the relation that the electric fields associated with the two Coulomb potentials are equal at the potential maximum

$$\frac{eZ}{b^2} = \frac{eZ_1}{(r-b)^2} \tag{8.85}$$

Thus the maximum quantum number is given by

$$n_m^2 = \frac{r}{2a_o}\,\frac{Z}{1 + 2\sqrt{Z_1/Z}} \tag{8.86}$$

If the ionized gas contains only one type of perturber, the average distance to a perturbing ion is given by a relation such as equation (8.81). Thus

$$n_m^2 \approx \frac{1}{2a_o}\left(\frac{3}{4\pi\rho_1}\right)^{1/3}\frac{Z}{1 + 2\sqrt{Z_1/Z}} = \frac{1}{2a_o}\left(\frac{3Z_1}{4\pi\rho_e}\right)^{1/3}\frac{Z}{1 + 2\sqrt{Z_1/Z}} \tag{8.87}$$

where ρ_e is the electron number density.

If several types of perturbers are present, the probability that no ion of type i, having a number density ρ_i, lies within the range of the quantum state n_m can be expressed as

$$P_i = exp\left(- \frac{4\pi}{3} \rho_i r_i{}^3\right) = exp\left[- \frac{4\pi\rho_i}{3} \left(\frac{2a_o n_m{}^2}{Z}\right)^3 \left(1 + 2\sqrt{Z_i/Z}\right)^3\right] \tag{8.88}$$

Then the probability that none of the perturbers of any type fall within the range of the quantum state n_m is the product

$$P = \prod_i P_i = exp\left[- \frac{4\pi}{3} \left(\frac{2a_o n_m{}^2}{Z}\right)^3 \sum_i \rho_i \left(1 + 2\sqrt{Z_i/Z}\right)^3\right] \tag{8.89}$$

In practice, Z_i and Z are usually about equal so the function $\left(1 + 2\sqrt{Z_i/Z}\right)^3$ is expanded about $Z_i/Z = 1$ to give

$$\left(1 + 2\sqrt{Z_i/Z}\right)^3 = 27 + 27\left(\frac{Z_i}{Z} - 1\right) + . . . \approx 27 \frac{Z_i}{Z} \tag{8.90}$$

$$P \approx exp\left[- \frac{4\pi}{3} \left(\frac{6a_o n_m{}^2}{Z}\right)^3 \sum_i \rho_i \frac{Z_i}{Z}\right] = exp\left[- \frac{4\pi}{3} \left(\frac{6a_o n_m{}^2}{Z^{4/3}}\right)^3 \rho_e\right] \tag{8.91}$$

The average value of the maximum quantum number n_m is approximately given when the exponent is -1, thus

$$n_m{}^2 \approx \frac{Z}{6a_o} \left(\frac{3Z}{4\pi\rho_e}\right)^{1/3} \tag{8.92}$$

and the average reduction in ionization potential is approximately

$$\Delta E = \frac{e^2 Z^2}{2a_o n_m{}^2} \approx 3e^2 Z \left(\frac{4\pi\rho_e}{3Z}\right)^{1/3} \tag{8.93}$$

The maximum quantum number in a high-density ionized gas is even less than above because of a Debye shielding effect that truncates the nuclear potential even sooner than a perturbing neighbor ion. A temperature effect then occurs because of changes in the distribution of charged particles in the gas with changes in temperature.

Consider the charge shielding about a test particle with charge Ze. The electric potential per unit charge is defined as ϕ and the charged particles are assumed to be distributed in an equilibrium Boltzmann distribution

$$\rho = \rho_e \, e^{e\phi/kT} \tag{8.94}$$

The electric potential is the solution to Poisson's equation

$$\nabla^2\phi = -4\pi\rho = -4\pi\left[Ze\delta(r) - e\rho_e\ e^{e\phi/kT} + e\sum_i Z_i\rho_i\ e^{-Z_i e\phi/kT}\right] \tag{8.95}$$

where $\delta(r)$ is the delta function, $\delta(0) = 1$, $\delta(r \neq 0) = 0$. At large r, the exponentials are expanded because $e\phi$ is then small compared with kT:

$$\nabla^2\phi = 4\pi e\left[\rho_e\left(1 + \frac{e\phi}{kT} + \ .\ .\ .\right) - \sum_i Z_i\rho_i\left(1 - \frac{Z_i e\phi}{kT} + .\ .\right)\right] \tag{8.96}$$

If the ionized gas is electrically neutral,

$$\rho_e = \sum_i Z_i\rho_i \tag{8.97}$$

Then equation (8.96) becomes, with radial symmetry included,

$$\frac{d^2\phi}{dr^2} + \frac{2}{r}\frac{d\phi}{dr} = \frac{4\pi e^2\phi}{kT}\left(\rho_e + \sum_i Z_i{}^2\rho_i\right) \tag{8.98}$$

A solution to equation (8.98) with the correct asymptotic limits at both large r and small r is

$$\phi = \frac{Ze}{r}\, exp\left(-\frac{r}{D}\right) \tag{8.99}$$

where the characteristic Debye length is given by

$$D^2 = \frac{kT}{4\pi e^2\left(\rho_\epsilon + \sum_i Z_i{}^2\rho_i\right)} \tag{8.100}$$

The effect of the Debye potential is to perturb the energy levels very little up to the point where $r < D$, but to truncate levels where $r >> D$. To a first approximation, the quantum levels are truncated where $r = D$ or

$$n_m{}^2 = \frac{ZD}{a_o} = \frac{Z}{a_o}\left[\frac{kT}{4\pi e^2\left(\rho_e + \sum_i Z_i\rho_i\right)}\right]^{1/2} \tag{8.101}$$

A more rigorous deviation given by Margenau and Lewis (ref. 8) is as follows.

The Schroedinger equation with the Debye potential is, in energy units of $e^2/2a_o$ and distance units of a_o,

$$-\nabla^2\psi - \frac{2Z}{r}\, e^{-r/D}\psi = E\psi \tag{8.102}$$

A small perturbation method will not apply because the levels near the series limit have energy the same order as the perturbations involved. Therefore, a variational method is used with hydrogen-like wave functions with an effective nuclear charge z as the variational parameter. The Laplacian operator acting on the hydrogen-like function ψ_n yields

$$-\nabla^2\psi_n = \left(E_n{}^o + \frac{2z}{r}\right)\psi_n \tag{8.103}$$

where $E_n{}^o = -z^2/n^2$ and n is the quantum number. Substitute equation (8.103) into equation (8.102), multiply by $\psi_n{}^*$, and integrate over all space, to obtain for the energy

$$E_n = E_n{}^o + 2\int \psi_n{}^* \left(\frac{z - Ze^{-r/D}}{r}\right)\psi_n \, d\tau \tag{8.104}$$

Since the wave function is of interest principally where $r < D$, the factors $e^{(-r/D)}$ are expanded in a power series to give

$$\int \frac{z - Ze^{-r/D}}{r}\psi_n{}^2 \, d\tau = \int \frac{z - Z}{r}\psi_n{}^2 \, d\tau + \int \frac{Z}{r}\sum_{i=1}^{\infty}\frac{(-1)^{i+1}}{i!}\left(\frac{r}{D}\right)^i \psi_n{}^2 \, d\tau \tag{8.105}$$

Thus the energy given by equation (8.104) is

$$E_n = -\frac{z^2}{n^2} + 2(z - Z)\left\langle\frac{1}{r}\right\rangle + 2\,\frac{Z}{D}\sum_{i=0}^{\infty}\frac{(-1)^i}{(i+1)!}\left\langle\left(\frac{r}{D}\right)^i\right\rangle \tag{8.106}$$

Now the value of r^{-1} is just z/n^2, and the other averages can all be evaluated in terms of the parameter $\beta = n^2/zD$. The energy of state n can be expressed as

$$E_n = \frac{z^2 - 2zZ}{n^2} + \frac{2Z}{D}S(\beta) \tag{8.107}$$

where $S(\beta)$ is the series

$$S(\beta) = \sum_{i=0}^{\infty}\frac{(-1)^i}{(i+1)!}\left\langle\left(\frac{r}{D}\right)^i\right\rangle \tag{8.108}$$

The first few moments of r are

$$\left\langle\left(\frac{r}{D}\right)^o\right\rangle = 1 \tag{8.109a}$$

$$\left\langle \left(\frac{r}{D}\right)^1 \right\rangle = \frac{n^2}{zD}\left[\frac{3}{2} - \frac{l(l + 1)}{n^2}\right] \tag{8.109b}$$

$$\left\langle \left(\frac{r}{D}\right)^2 \right\rangle = \frac{n^4}{z^2D^2}\left[\frac{5}{2} - \frac{l(l + 1) - \frac{1}{3}}{n^2}\right] \tag{8.109c}$$

and for s states ($l = 0$), the function $S(\beta)$ becomes

$$S(\beta) = 1 - \frac{3}{4}\beta + \frac{5}{12}\beta^2 - \frac{35}{192}\beta^3 + \frac{63}{960}\beta^4 - \ldots \tag{8.108a}$$

The variational constraint that the best wave function gives the minimum energy leads to

$$\frac{1}{2}\frac{dE_n}{dz} = \frac{z - Z}{n^2} + \frac{Z}{D}\frac{dS}{d\beta}\frac{d\beta}{dz} = 0 \tag{8.110}$$

$$z - Z - Z\beta^2\frac{dS}{d\beta} = 0 \tag{8.111}$$

For the last bound quantum state,

$$E_{n_m} = z_m{}^2 - 2z_mZ + 2\beta_m z_m Z S(\beta_m) = 0 \tag{8.112}$$

Equations (8.111) and (8.112) give two equations in two unknowns z_m and β_m to be solved. To terms of first order, $S = 1$, $S' = 0$, $z_m = Z$, and $\beta_m = 1/2$. Then $n_m{}^2 = ZD/2a_o$, half the value given in equation (8.101). More precisely, Z can be eliminated from equations (8.111) and (8.112) to give

$$1 - 2\beta_m S - \beta_m{}^2 S' = 0 \tag{8.113}$$

For the s states where $S(\beta)$ is given by equation (8.108a), equations (8.111) and (8.112) are found to have roots where $\beta_m \simeq 1.1$ and $z_m \simeq 0.83Z$, in which case

$$\beta_m \simeq 1.1 \simeq \frac{n_m{}^2 a_o}{z_m D} \simeq \frac{n_m{}^2 a_o}{0.83ZD} \tag{8.114}$$

nearly the same result as equation (8.101).

The reduction in the ionization potential given by Debye shielding is just

$$\Delta E = -\frac{Z^2}{n_m^2} = -\frac{Z}{(\beta_m z_m)\left(\frac{D}{a_o}\right)} \tag{8.115}$$

where the product $(\beta_m z_m)$ is unity in the simple approximation given by equation (8.101) and is about 0.91 for *s* states as given by the more rigorous solution, equation (8.114).

The above estimates for the depression of the ionization potential and truncation of the electronic partition function are appropriate when the perturbing ions are slow moving compared with the motion of the bound electrons about their central nuclei. However, free electrons in a plasma often move with velocities comparable to those of the bound electrons; then an impact approximation is used to analyze the effect of electron collisions.

According to the uncertainty principle, the energy spread associated with the finite lifetime of a quantum state θ^{-1} is $h\theta$, and this is again related to the maximum quantum number, n_m, where the spacing between excited hydrogen-like levels equals the collision broadening, and the excited electron can escape to a continuum:

$$\Delta E = \left(\frac{dE}{dn}\right)_{n_m} = \frac{e^2 Z^2}{a_o n_m^3} = h\theta \tag{8.116a}$$

In the present case, the lifetime is established by the frequency of electron collisions strong enough to change the quantum state

$$\theta = \rho_e S \bar{v} \tag{8.117}$$

where ρ_e is the electron number density, S is the effective collision cross section, and $\bar{v}$ is the mean collision velocity $(8kT/\pi\mu)^{1/2}$. The reduced mass μ is essentially the electron mass in the present case since the atomic particles are so much heavier than the electron.

The cross section is estimated by calculating the total phase shift produced in a single encounter by the first-order Stark effect, and when this phase shift exceeds the order of 1 radian, this is deemed sufficient to disrupt the quantum state. Most of the collisions involved are distant ones and, in this case, to a first approximation, the free electron follows a straight-line trajectory with miss distance b (fig. 8.6). The perturbation of hydrogen-like orbits by the Stark effect has been worked out in detail by Bethe and Salpeter (ref. 3) and, in the field of the electron e^2/r^2, the interaction energy is

$$\Delta E = \pm \frac{3}{2}\frac{a_o e^2}{Z r^2} j \approx \pm \frac{a_o e^2}{2 Z r^2} n^2 \tag{8.116b}$$

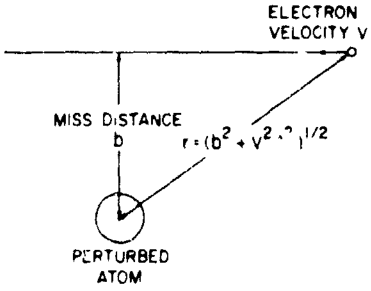

Figure 8.6.- Distant electron collision trajectory with respect to perturbed atom.

where j is an integer that takes all values from 0 to $n(n - 1)$. The average value of j for a given quantum state n is about $n^2/3$. The total phase shift produced over the duration of the encounter is then

$$\eta = \int_{-\infty}^{\infty} \frac{\Delta E}{\hbar}\, dt = \frac{a_o e^2 n^2}{2Z\hbar} \int_{-\infty}^{\infty} \frac{dt}{b^2 + v^2 t^2} = \frac{\pi a_o e^2 n^2}{2Zb\bar{v}\hbar} \tag{8.118}$$

The cross section is evaluated for the radius b_o where η is approximately unity:

$$S = \pi b_o^2 \approx \frac{\pi^3 a_o^2 e^4 n^4}{4Z^2 \bar{v}^2 \hbar^2} \tag{8.119}$$

and the appropriate collision frequency is

$$\theta = \frac{\pi^3 a_o^2 e^4 n^4 \rho_e}{4Z^2 \hbar^2 \bar{v}} \tag{8.120}$$

Let $n = n_m$ in equation (8.1 [illegible] and solve simultaneously with equation (8.116a) to obtain

$$n_m^7 = \frac{2Z^4 \hbar \bar{v}}{\pi^4 e^2 a_o^3 \rho_e} \tag{8.121}$$

In any given ionized gas, the cutoff quantum number is the lowest of those given for static ion perturbations, equation (8.92); for Debye shielding effects, equation (8.101); and for electron impact perturbations, equation (8.121). At moderate temperatures, kT about one-half to one eV, the electron impact broadening generally produces the lowest cutoff at low densities, though the ionization potential decrease produced by positive ion perturbation effects gives about the same value. As density is increased, the Debye shielding effect which varies much more strongly with density (as $\rho^{-1/4}$) becomes the dominant one at these temperatures. However, as temperature increases further, the Debye cutoff which also varies as $T^{1/4}$, becomes large enough that it no longer influences the phenomenon. At very high temperatures, kT greater than one eV or more, the electron impact cutoff, which depends very weakly on temperature, may become large enough that the ion perturbation effects provide the lowest value of n_m.

Many additional theories have been proposed. Ecker and Weizel (ref. 9) treat an ionized gas as a modified Debye-Hickel electrolyte. Griem (ref. 10) uses the Debye potential to determine a minimized free energy. A good review of these theories and others is given by Drawin and Felenbok (ref. 11). Also, any theory of spectral line broadening can be applied to the reduction of the ionization potential as well. Aller (ref. 12) reviews some of the line-broadening theories as does Margenau and Lewis (ref. 8). Simple approximations for electron impact and ion Stark broadening are given by Hansen (ref. 13). These theories even with attempts at considerably more rigor, all give somewhat similar results. Thus, the qualitative descriptions of ionization lowering are probably adequate, although one should certainly expect the quantitative results to be somewhat approximate.

8.11 CONCLUDING REMARKS

Effects of vibration-rotation coupling in diatomic molecules, dispersion forces in gases, and electronic state perturbations in gases have been treated in a very approximate manner. However, this is often sufficient to correct the partition functions since, for gases that are not too dense, the uncoupled mode approximation gives partition functions that are already reasonably accurate. The general methods presented here for correcting the partition function can be extended to other cases of intermode coupling, and also permit one to follow the development of more precise models where required.

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CHAPTER 9 - EQUILIBRIUM PROPERTIES OF CHEMICALLY REACTING GASES

9.1 SUMMARY

The equilibrium energy, enthalpy, entropy, specific heats at constant volume and constant pressure, and the equation of state of the gas are all derived for chemically reacting gas mixtures in terms of the compressibility, the mol fractions, the thermodynamic properties of the pure gas components, and the change in zero point energy due to reaction. Results are illustrated for a simple diatomic dissociation reaction and nitrogen is used as an example. Next, a gas mixture resulting from combined diatomic dissociation and atomic ionization reactions is treated and, again, nitrogen is used as an example. A short discussion is given of the additional complexities involved when precise solutions for high-temperature air are desired, including effects caused by NO produced in shuffle reactions and by other trace species formed from CO_2, H_2O, and Ar found in normal air.

9.2 INTRODUCTION

All previous chapters have led us to the point where we can accurately calculate the equilibrium thermodynamic properties of most atomic and molecular species that occur in usual gases and plasmas, and also the equilibrium constants for chemical reactions that may occur between any of these species. Thus we can now calculate the equilibrium properties of chemically reacting gases. Consider first a single-chemical reaction and then proceed to overlapping reactions where the simultaneous solution of more than one chemical balance equation is required.

9.3 GENERAL RELATIONS IN CHEMICALLY REACTING GASES

The chemical reaction is written in the form

$$\sum_i a_i A_i = 0 \tag{9.1}$$

where the factors a_i are the stoichiometric coefficients for the species A_i involved in the reaction. The species with positive coefficients are considered the reactants and those with negative coefficients are products.

Although equation (9.1) is conventionally called a reaction equation, it should really be termed a chemical balance equation. The equilibrium properties of a gas mixture do not depend on the reaction path, and the set of chemical equations chosen to introduce the balance between species need not correspond to the most probable path. The actual reactions leading to the various species typically require multistep collision processes that involve a variety of excited rotational, vibrational, or electronic states rather than a simple, single-step process as suggested by many common reaction equations. However, the convention is firmly entrenched that the term reaction is used to signify the transition from reactants to products by whatever means.

The equilibrium constant for the chemical equation may be expressed either in terms of partial pressures p_i or in terms of concentrations, usually mol concentrations n_i. The former,

$$K_p = \prod_i p_i^{-a_i} \tag{9.2}$$

is most useful whenever properties are to be evaluated as functions of pressure and temperature; the latter

$$K_c = \prod_i n_i^{-a_i} \tag{9.3}$$

is most useful when properties are to be evaluated as functions of density and temperature.

Partition functions for each species involved evaluated at unit pressure, usually 1 atm, are used to determine K_p; partition functions evaluated at unit mol concentration are used to determine K_c. The pressure standardized partition function Q_p is thus related to the complete partition function Q:

$$Q_p = pQ \tag{9.4}$$

while the concentration standardized partition function Q_c is

$$Q_c = \frac{p}{RT} Q = \frac{Q_p}{RT} \tag{9.5}$$

The equilibrium constants in terms of these standardized partition functions are just

$$K_p = e^{-\Delta E_0/RT} \prod_i [Q_p(A_i)]^{-a_i} \tag{9.6}$$

$$K_c = e^{-\Delta E_0/RT} \prod_i [Q_c(A_i)]^{-a_i} = K_p(RT)^{-\Delta n} \tag{9.7}$$

where the change in zero point energy created by the reaction is

$$\Delta E_O = -\sum_i a_i E_O(A_i) \tag{9.8}$$

and Δn is the total number of mols changed in the reaction

$$\Delta n = -\sum_i a_i \tag{9.9}$$

Since only differences of energy are involved, the reference energy can be established in any consistent way. Conventionally, the zero point energies E_O of atomic or homonuclear molecular species that are stable at STP (273.1° K, 1 atm) are taken to be zero; then the zero point energies of the remaining species are adjusted accordingly. For example, N_2 is stable at standard conditions and is given the value zero for E_O (N_2), ignoring essentially constant factors such as nuclear spin and ground state vibrational energy. Then the value of $E_O(N)$, the zero point energy of the N atoms, is half the dissociation energy of N_2. Compounds such as NO have values for E_O equal to the heat of formation from the homonuclear molecular species, in this case, N_2 and O_2. Electrons are taken to have a zero value for E_O and the entire energy of ionization is assigned to E_O for the ionized particles; thus there is no differentiation between electrons formed in single-, double-, and triple-, and higher-order ionization processes.

The equilibrium constant in equation (9.2), expressed in terms of mol fractions x_i and total pressure p, is

$$K_p = p^{\Delta n} \prod_i x_i^{a_i} \tag{9.10}$$

For $\Delta n = 0$, such as for a simple exchange reaction $A + BC \rightarrow AB + C$, K_p is independent of pressure. For reactions such as dissociation, $A_2 \rightarrow 2A$, or ionization, $A \rightarrow A^+ + e$, $\Delta n = 1$ and K_p is proportional to the first power of pressure. Other Δn values are possible for reactions in general, of course

The sum of mol fractions is unity, by definition:

$$\sum_i x_i = 1 \tag{9.11}$$

Equation (9.10) and (9.11) provide two independent equations for the unknowns x_i. If only two-component species are involved, as in dissociation, this is sufficient to solve for both x_i. If more than two species are present, the remaining equations needed are provided by the conservation of mass or charge involved. For example, the simple ionization reaction $A \rightarrow A^+ + e$ involves three species, and the third independent equation is then given by charge conservation:

$$x(A^+) = x(e) \tag{9.12}$$

As another example, the exchange reaction $A + BC \rightarrow AB + C$ involves four species; two independent equations are provided by conservation of the ratios of atomic species A to B and A to C for a given starting mixture of the gas:

$$\frac{x(A) + x(AB)}{x(BC) + x(AB)} = \gamma_{A:B} \tag{9.13a}$$

$$\frac{x(A) + x(AB)}{x(BC) + x(C)} = \gamma_{A:C} \tag{9.13b}$$

The mass ratios $\gamma_{A:B}$ and $\gamma_{A:C}$ are known initial conditions; equations (9.13a) and (9.13b) coupled with equation (9.10) and (9.11) provide the four equations needed to solve for the four unknown mol fractions in this case. If additional atomic species were involved, then additional equations such as (9.13) would exist which specify the atomic ratios given by the initial conditions.

The above equations are solved for the mol fractions x_i in terms of either p and K_p or n and K_c, depending on whether the properties are to be evaluated at a given p and T or a given ρ and T. In addition, the derivatives $(\partial x_i/\partial T)_p$ and $(\partial x_i/\partial T)_\rho$ required to evaluate the specific heats are found from the solutions for the x_i.

At normal densities or densities larger by two to three orders of magnitude, the gas is dilute enough that each component behaves as an ideal gas. Then the equation of state can be expressed as

$$\frac{p}{\rho} = \frac{RT}{\overline{M}} = \frac{RT}{\sum\limits_i x_i M_i} = Z\,\frac{RT}{M_o} \tag{9.14}$$

The quantity Z is called the compressibility; at very high densities, compressibility reflects the effects of intermolecular forces, but here it represents the number of mols of gas produced by chemical reaction from each mol of gas present at some initial condition where the average molecular weight is M_o:

$$Z = \frac{M_o}{\overline{M}} = \left[\sum_i x_i \left(\frac{M_i}{M_o}\right)\right]^{-1} \tag{9.15}$$

By convention, M_o is taken to be the average molecular weight of the equilibrium gas mixture at standard conditions (273° K and 1 atm pressure). For many applications, properties such as energy, entropy, and specific heat are most useful when evaluated for a fixed quantity of gas rather than for a mol, since a mol of chemically reacting mixture may represent a changing amount of gas. The amount of gas in Z mols is a fixed quantity, so the thermodynamic properties are evaluated for Z mols. The dimensionless energy and enthalpy in Z

mols of gas mixture are (see eq. (1.73))

$$\frac{ZE}{RT} = Z\sum_i x_i \left(\frac{E}{RT}\right)_i = Z\sum_i x_i \left[T\frac{d\ ln\ Q_c(A_i)}{dT} + \frac{E_o(A_i)}{RT}\right] \tag{9.16}$$

$$\frac{ZH}{RT} = Z\sum_i x_i \left(\frac{H}{RT}\right)_i = Z\sum_i x_i \left[T\frac{d\ ln\ Q_p(A_i)}{dT} + \frac{E_o(A_i)}{RT}\right]$$

$$= Z\sum_i x_i \left[T\frac{d\ ln\ Q_c(A_i)}{dT} + 1 + \frac{E_o(A_i)}{RT}\right] = \frac{ZE}{RT} + Z \tag{9.17}$$

The dimensionless entropy in Z mols of gas mixture is (see problem 1.6)

$$\frac{ZS}{R} = Z\left[\sum_i x_i \left(\frac{S}{R}\right)_i - \sum_i x_i\ ln\ x_i\right]$$

$$= Z\left\{\sum_i x_i \left[T\frac{d\ ln\ Q_p(A_i)}{dT} + ln\ Q_p(A_i)\right] - \sum x_i\ ln\ x_i - ln\ p\right\} \tag{9.18}$$

where the component mol entropies $(S/R)_i$ are evaluated at the total pressure p. The term $\sum_i x_i\ ln\ x_i$, often referred to as the entropy of mixing, simply represents the correction required to transform the component mol entropies to the actual partial pressures involved.

Specific heats involve one additional complication; the derivatives of the mol fractions are required in addition to the mol fractions themselves. The dimensionless specific heat at constant volume is given by

$$\frac{ZC_v}{R} = \frac{d}{dT}\left(\frac{ZE}{R}\right) = \sum_i \left[Zx_i \frac{d}{dT}\left(\frac{E}{R}\right)_i + \left(\frac{E}{R}\right)_i \left(\frac{\partial Zx_i}{\partial T}\right)_\rho\right]$$

$$= \sum_i \left\{Zx_i \frac{d}{dT}\left[T^2\frac{d\ ln\ Q_c(A_i)}{dT}\right] + \left(\frac{\partial Zx_i}{\partial T}\right)_\rho \left[T^2\frac{d\ ln\ Q_c(A_i)}{dT} + \frac{E_o(A_i)}{R}\right]\right\} \tag{9.19}$$

The dimensionless specific heat at constant pressure is given by a similar expression

$$\frac{ZC_p}{R} = \frac{d}{dT}\left(\frac{ZH}{R}\right) = \sum_i \left[Zx_i \frac{d}{dT}\left(\frac{H}{R}\right)_i + \left(\frac{H}{R}\right)_i \left(\frac{\partial Zx_i}{\partial T}\right)_p\right]$$

$$= \sum_i \left\{Zx_i \frac{d}{dT}\left[T^2\frac{d\ ln\ Q_p(A_i)}{dT}\right] + \left(\frac{\partial Zx_i}{\partial T}\right)_p \left[T^2\frac{d\ ln\ Q_p(A_i)}{dT} + \frac{E_o(A_i)}{R}\right]\right\} \tag{9.20}$$

Because of the relation between the pressure standardized and concentration standardized partition functions, the component energies and enthalpies and the component specific heats are related simply by

$$\left(\frac{H}{RT}\right)_i = \left(\frac{E}{RT}\right)_i + 1 \tag{9.21}$$

$$\left(\frac{C_p}{R}\right)_i = \left(\frac{C_v}{R}\right)_i + 1 \tag{9.22}$$

Thus the total enthalpy of the mixture can be obtained simply from the total energy

$$\frac{ZH}{RT} = \frac{ZE}{RT} + Z \tag{9.23}$$

and vice versa. The difference between the total specific heats is no longer the gas constant, however, but

$$\frac{C_p - C_v}{R} = 1 + \frac{T}{Z}\sum_i \left[\left(\frac{H}{RT}\right)_i \left(\frac{\partial Zx_i}{\partial T}\right)_p - \left(\frac{E}{RT}\right)_i \left(\frac{\partial Zx_i}{\partial T}\right)_\rho\right] \tag{9.24}$$

The products Zx_i can often be expressed as relatively simple functions of the fraction of reactant species transformed to product species by reaction. The derivatives at constant pressure and constant density can be related to the derivatives $(d\ ln\ K_p/dT)$ and $(d\ ln\ K_c/dT)$, respectively. According to equation (9.6) and (9.7),

$$\begin{aligned} T\frac{d\ ln\ K_p}{dT} &= \frac{\Delta E_o}{RT} - \sum_i a_i \left[T\frac{d\ ln\ Q_p(A_i)}{dT}\right] \\ &= \frac{\Delta E_o}{RT} - \sum_i a_i \left(\frac{H - E_o}{RT}\right)_i \end{aligned} \tag{9.25}$$

$$\begin{aligned} T\frac{d\ ln\ K_c}{dT} &= \frac{\Delta E_o}{RT} - \sum_i a_i \left[T\frac{d\ ln\ Q_c(A_i)}{dT}\right] \\ &= \frac{\Delta E_o}{RT} - \sum_i a_i \left(\frac{E - E_o}{RT}\right)_i \\ &= T\frac{d\ ln\ K_p}{dT} - \Delta n \end{aligned} \tag{9.26}$$

9.4 DISSOCIATION OF DIATOMIC MOLECULES

Consider the simple dissociation reaction

$$A_2 \rightleftharpoons 2A \tag{9.27}$$

The pressure standardized equilibrium constant for this reaction is

$$K_f = \frac{[Q_p(A)]^2}{Q_p(A_2)} e^{-D/kT} \tag{9.28}$$

where D is the dissociation energy. Let f be the fraction of A_2 that is dissociated and x, the mol fraction of A formed; then $(1-x)$ is the mol fraction of A_2 remaining:

$$\left.\begin{aligned} x &= \frac{2f}{(1+f)} \\ 1 - x &= \frac{(1-f)}{(1+f)} \end{aligned}\right\} \tag{9.29}$$

The compressibility Z is the number of mols of gas produced per initial mol of A_2:

$$Z = 1 + f = \frac{2}{(2 - x)} \tag{9.30}$$

The fraction f, or the mol fraction x, is determined from the relation between the equilibrium constant and the particle pressures

$$K_p = \frac{p(A^2)}{p(A_2)} = \frac{x^2 p}{1 - x} = \frac{4f^2}{1 - f^2} p \tag{9.31}$$

$$f = \left(\frac{K_p}{4p + K_p}\right)^{1/2} \tag{9.32}$$

With f determined, the dimensionless enthalpy in Z mols of the dissociated gas is simply (see eq. (9.17))

$$\frac{ZH}{RT} = Z(1 - x)\left(\frac{H}{RT}\right)_{A_2} + Zx\left(\frac{H}{RT}\right)_A$$

$$= (1 - f)\left(\frac{H}{RT}\right)_{A_2} + 2f\left(\frac{H}{RT}\right)_A \tag{9.33}$$

while the dimensionless entropy is (see eq. (9.18))

$$\frac{ZS}{R} = Z\left[(1-x)\left(\frac{S}{R}\right)_{A_2} + x\left(\frac{S}{R}\right)_A - (1-x)\ln(1-x) - x \ln x - \ln p\right]$$

$$= (1-f)\left(\frac{S}{R}\right)_{A_2} + 2f\left(\frac{S}{R}\right)_A - (1-f)\ln(1-f) - 2f\ln(2f) + (1+f)\ln(1+f) - \ln p \tag{9.34}$$

and the specific heat at constant pressure is (see eq. (9.20))

$$\frac{ZC_p}{R} = Z\left\{(1-x)\left(\frac{C_p}{R}\right)_{A_2} + x\left(\frac{C_p}{R}\right)_A + \left(\frac{H}{RT}\right)_{A_2}\left[T\frac{\partial Z(1-x)}{\partial T}\right]_p + \left(\frac{H}{RT}\right)_A\left(T\frac{\partial Zx}{\partial T}\right)_p\right\}$$

$$= (1-f)\left(\frac{C_p}{R}\right)_{A_2} + 2f\left(\frac{C_p}{R}\right)_A + \left(T\frac{\partial f}{\partial T}\right)_p\left[2\left(\frac{H}{RT}\right)_A - \left(\frac{H}{RT}\right)_{A_2}\right] \tag{9.35}$$

The last term in equation (9.35) is approximately the product of $(\partial f/\partial \ln T)_p$ and D/kT since

$$2\left(\frac{H}{RT}\right)_A - \left(\frac{H}{RT}\right)_{A_2} = \frac{D}{kT} + 2T\frac{d\ln Q_p(A)}{dT} - T\frac{d\ln Q_p(A_2)}{dT} \tag{9.36}$$

and D/kT is much larger than the derivatives that follow.

The specific heat at constant volume is given by an expression similar to equation (9.35):

$$\frac{ZC_v}{R} = (1-f)\left(\frac{C_v}{R}\right)_{A_2} + 2f\left(\frac{C_v}{R}\right)_A + \left(T\frac{\partial f}{\partial T}\right)_\rho\left[2\left(\frac{E}{RT}\right)_A - \left(\frac{E}{RT}\right)_{A_2}\right] \tag{9.37}$$

The fractions f and x behave something like step functions, starting at zero at very low temperature, rising rapidly in the reaction region of temperature where D/kT is the order of 10, and asymptotically approaching unity at high temperature. Thus the derivatives $(\partial f/\partial \ln T)$ are sharply peaked in this region and the last terms in equations (9.35) and (9.37) dominate, because of the peaked derivative *and* the large value of D/kT. The specific heats are thus sharply peaked also. The derivative $(\partial f/\partial \ln T)_p$ is, according to equations (9.32) and (9.25),

$$\left(\frac{\partial f}{\partial \ln T}\right)_p = \frac{f}{2}(1-f^2)T\frac{d\ln K_p}{dT}$$

$$= \frac{f}{2}(1-f^2)\left[\frac{D}{kT} + 2T\frac{d\ln Q_p(A)}{dT} - T\frac{d\ln Q_p(A_2)}{dT}\right] \tag{9.38}$$

To evaluate the properties above at given density and temperature, the concentration standardized equilibrium constant is used, a quantity expressible in terms of the number of mols per unit volume,

$$n = \frac{\rho}{\bar{M}} = \frac{\rho Z}{M_o} \tag{9.39}$$

$$K_c = \frac{x^2 n}{1 - x} = \frac{4f^2}{1 - f}\frac{\rho}{M_o} \tag{9.40}$$

In this case, the solution for f is a slightly more complex quadratic relation

$$f = -\frac{K_c M_o}{8\rho} + \sqrt{\left(\frac{K_c M_o}{8\rho}\right)^2 + \frac{K_c M_o}{4\rho}} \tag{9.41}$$

From equations (9.40) and (9.26), the derivative $(\partial f/\partial \ln T)_\rho$ is

$$\left(T \frac{\partial f}{\partial T}\right)_\rho = \frac{f(1 - f)}{(2 - f)} T \frac{d \ln K_c}{dT}$$

$$= \frac{f(1 - f)}{(2 - f)} \left[\frac{D}{kT} + 2T \frac{d \ln Q_c(A)}{dT} - T \frac{d \ln Q_c(A_2)}{dT}\right] \tag{9.42}$$

9.5 DISSOCIATION OF N_2

To illustrate the above calculations, dissociation of pure N_2 is used as the example. The calculations are simplified by truncating the electronic partition functions after the first few low-lying terms and by neglecting all interaction terms between electronic, vibrational, and rotational energy.

Problem 9.1: Show that the logarithm of the translational partition function for 1 atm of pressure is

$$Q_p = \frac{5}{2} \ln T + \frac{3}{2} \ln M - 3.6651 \tag{9.43}$$

where T is in °K and M is the molecular weight in atomic mass units (1.6597×10^{-24} gm).

The logarithms of the partition functions involved in the nitrogen dissociation calculation are approximately

$$\ln Q_p(N_2) \approx \frac{7}{2} \ln T - 0.422 - \ln\left(1 - e^{-3395/T}\right) \tag{9.44}$$

$$\ln Q_p(N) \approx \frac{5}{2} \ln T + 0.293 + \ln\left(4 + 10e^{-27,660/T} + 6e^{-41,500/T}\right) \tag{9.45}$$

and the equilibrium constant in pressure units is

$$ln\ K_p = -\frac{113,250}{T} + 2\ ln\ Q_p(\mathrm{N}) - ln\ Q_p(\mathrm{N_2}) \tag{9.46}$$

The component energies are

$$\left(\frac{E - E_o}{RT}\right)_{\mathrm{N_2}} = \frac{5}{2} + \frac{3,395}{T}\left(e^{3,395/T} - 1\right)^{-1} \tag{9.47}$$

$$\left(\frac{E - E_o}{RT}\right)_{\mathrm{N}} = \frac{3}{2} + \frac{10\left(\frac{27,660}{T}\right)e^{-27,660/T} + 6\left(\frac{41,500}{T}\right)e^{-41,500/T}}{4 + 10e^{-27,660/T} + 6e^{-41,500/T}} \tag{9.48}$$

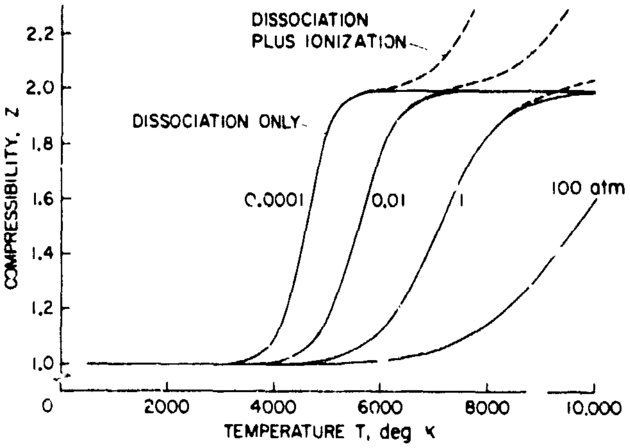

Figure 9.1.- Compressibility of nitrogen (—— dissociation only, ---- dissociation plus ionization).

Results of calculations for pressures of 10^{-4}, 10^{-2}, 1, and 10^2 atm are shown in figure 9.1 for compressibility. The compressibility is unity until dissociation starts at temperatures about 4000° to 7000° K, depending on pressure. The reaction is inhibited at the higher pressures according to the law of mass action because two mols of product species are produced from each mol of reactant. The compressibility asymptotically approaches two as the dissociation proceeds to completion. As temperature increases further, the atoms are ionized. The dotted lines show the effect of including the ionization reactions (discussed subsequently) and indicate the limits of validity for the model which treats nitrogen as a gas with the single dissociation reaction.

The dimensionless enthalpy, ZH/RT, in Z mols of the $\mathrm{N_2}$ and N mixture is graphed in figure 9.2. This ratio increases slightly at low temperature because of the excitation of vibrational energy in the molecules, independently of pressure. The enthalpy jumps upward as the atoms appear with their large zero point energy $D/2$. As the dissociation proceeds to completion, the ratio tends toward the limit $3/2 + D/2kT$, except that electronic excitation begins to assume some importance and, as the dotted curves show, the ionization reactions begin to have large effects at high T.

The entropy ratio S/R for dissociating nitrogen is shown in figure 9.3. Entropy increases smoothly with temperature except for the jump that appears in the temperature interval where dissociation occurs. Another jump appears as the ionization reactions occur (dotted lines).

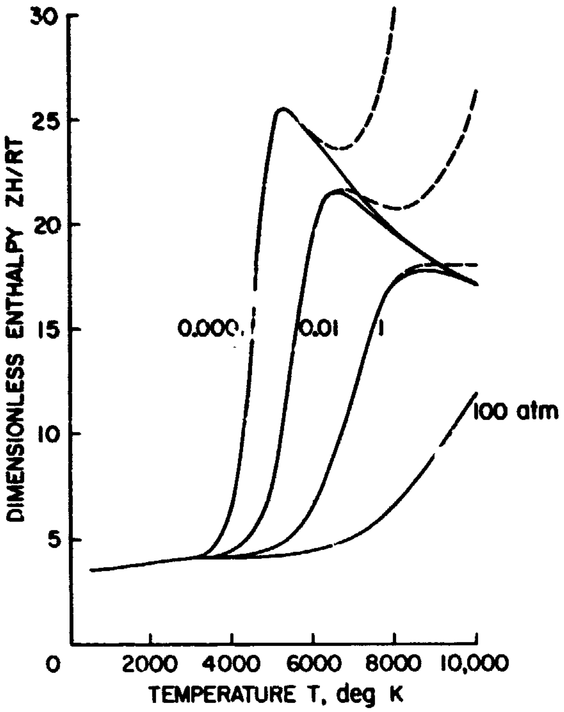

Figure 9.2.- Enthalpy of nitrogen (—— dissociation only, ---- dissociation plus ionization).

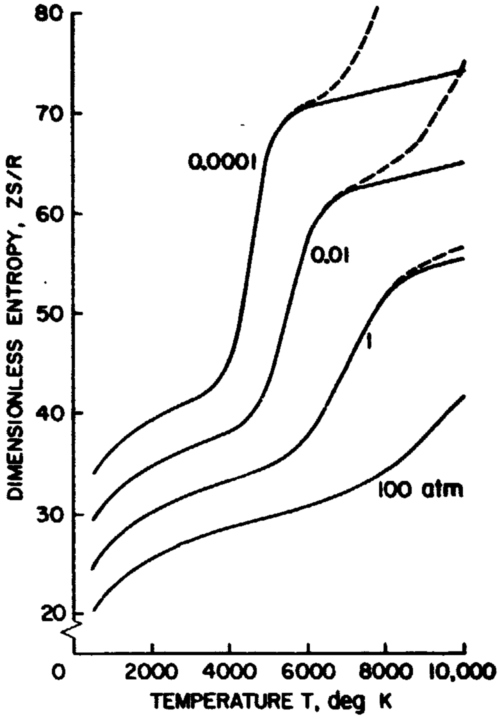

Figure 9.3.- Entropy of nitrogen (—— dissociation only, ---- dissociation plus ionization).

Specific heat at constant pressure and the ratio of specific heats are shown in figures 9.4 and 9.5, respectively. The specific heat increases slightly at low temperature from $5R/2$ to $7R/2$ as the molecular vibrational energy is excited. Then, as the dissociation reaction appears, the specific heat goes through a very large maximum, principally because of the peak in the term $(D/2)(\partial Zx/\partial T)_p$, that is, the product of atomic internal energy and mol fraction derivative. The effect of ionization reactions is not indicated, but the reader can predict that another large peak will occur where the slope of the compressibility curve (fig. 9.6) goes through another maximum. This peak will be even larger than that due to dissociation because the internal energy of the N^+ ions is even larger

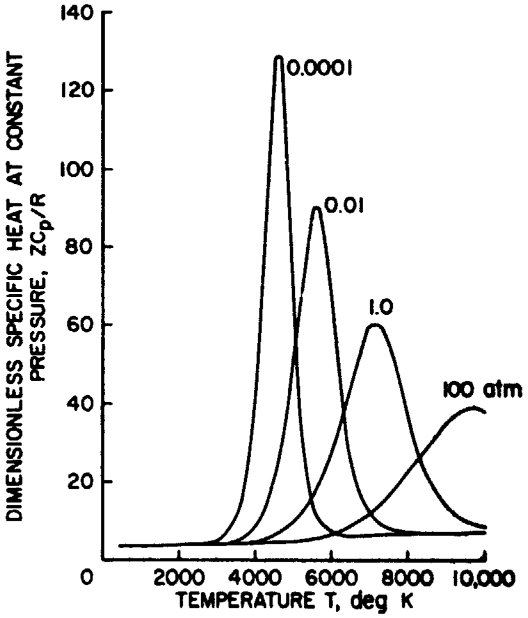

Figure 9.4.- Specific heat at constant pressure for dissociating nitrogen.

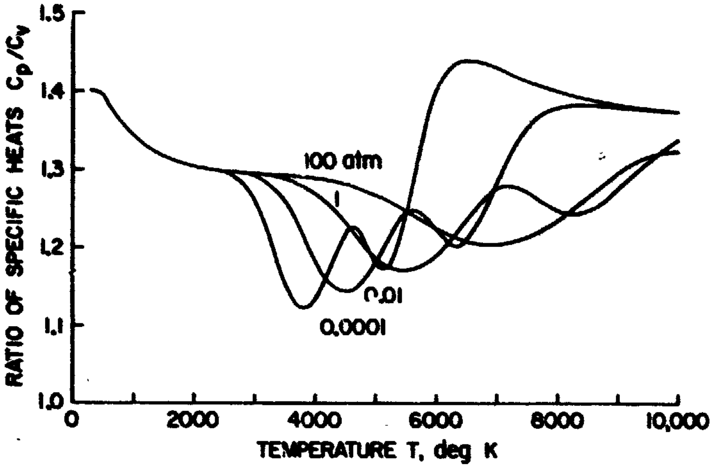

Figure 9.5.- Ratio of specific heats for dissociating nitrogen.

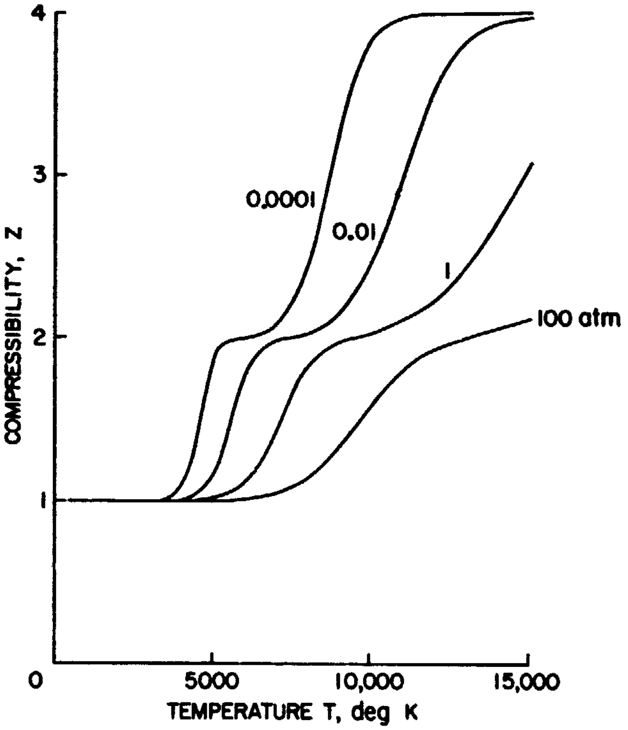

Figure 9.6.- Compressibility of dissociating, ionizing nitrogen.

than that of the atoms - namely the sum of $D/2$ plus the ionization energy I.

The ratio of specific heats shown in figure 9.5 starts near 7/5, the value for rigid diatomic rotators, decreases to 9/7 as the vibrations are excited, then drops further as the specific heats increase. The maximum in C_v occurs at slightly lower temperature than the maximum in C_p, so the ratio takes an extra "wiggle" near the minimum and then finally rises to the pure monatomic gas value. This value would be 5/3 except that the contribution of the electronic partition function for atomic nitrogen becomes appreciable at this point. The ionization reactions also create additional effects at those temperatures where the deviations from the pure dissociating gas model are indicated in figures 9.1 and 9.2.

9.6 COMBINED DISSOCIATION AND IONIZATION

As indicated previously, the ionization reactions, as well as the dissociation reaction, must be considered at higher temperatures. The simple diatomic gas becomes a complex chemical mixture with the following reactions:

$$A_2 \rightleftarrows 2A \tag{9.49a}$$

$$A + A \rightleftarrows A_2^+ + e \tag{9.49b}$$

$$A \rightleftarrows A^+ + e \tag{9.49c}$$

$$A^+ \rightleftarrows A^{++} + e \tag{9.49d}$$

Exact solutions for the mol fractions of the species involved requires simultaneous solutions of several nonlinear equations, which can be accomplished with good accuracy on electronic computers by iterative methods. In many cases, the reactions can be decoupled to a good approximation because the ionization energies are typically much larger than the dissociation energy. For example, dissociation energies are typically the order of 5 to 10 eV, while the single ionization energies are the order of 15 eV, and multiple ionization energies increase many electron volts for each additional electron removed. Except at very high pressures, the order of 10^3 atm or more, these reactions can be treated as though one is complete before the next begins. At high pressures, the reaction zones spread over broader ranges of temperature until appreciable overlapping occurs. Even then, the solutions can usually be approximated very well by treating only two or three reactions simultaneously rather than the entire set.

To illustrate the decoupled reaction approximation, consider solutions to equations (9.49) by this method. First, equation (9.49b) is ignored initially because the fraction of molecular ions, A_2^+, is typically very small compared with the other species and does not significantly influence the thermodynamic properties. This species is added later by a small perturbation of the first-order solution for the major species. The remaining reactions are decoupled to a good approximation. We consider ionization only up to A^{++}, which is sufficient for temperatures up to 15,000° K in a typical case such as nitrogen, but the reader can readily extend the method to include higher-order ionization if desired for still higher temperatures. Let f_1 be the fraction of molecules dissociated; f_2, the fraction of atoms singly ionized; and f_3, the fraction of singly-charged ions that are doubly ionized. The compressibility is the number of moles produced from each mol of A_2 and can be expressed in the decoupled approximation

$$Z = 1 + f_1 + 2f_2 + 2f_3 \tag{9.50}$$

The pressure standardized equilibrium constants for the dissociation reaction, the single-ionization reaction, and the double-ionization reaction are designated K_α, K_β, and K_γ, respectively:

$$K_\alpha = \frac{x_A{}^2}{x_{A_2}} p \approx \frac{4f_1{}^2}{1 - f_1{}^2} p \tag{9.51a}$$

$$K_\beta = \frac{x_{A+}x_e}{x_A} p \approx \frac{f_2{}^2}{1 - f_2{}^2} p \tag{9.51b}$$

$$K_\gamma = \frac{x_{A++}x_e}{x_{A+}} p \approx \frac{f_3(1 + f_3)}{(2 + f_3)(1 - f_3)} p \tag{9.51c}$$

In the right-hand expressions for K_α, K_β, and K_γ, we have assumed that $Z = 1 + f_1$ for equation (9.51a), $Z = 2(1 + f_2)$ for equation (9.51b), and $Z = 2(2 + f_3)$ for equation (9.51c) so that the equations can be decoupled. The mol fraction of electrons in the last equation is $x_e = 2(1 + f_3)/Z$ since the electrons formed in the previous single-ionization reaction must also be counted. The reader can readily extend the procedures to triple, quadruple, and higher-order ionization.

The solution to equation (9.51a) is the same as for equation (9.32) used previously for the pure dissociating gas model:

$$f_1 = \left(\frac{K_\alpha}{4p + K_\alpha}\right)^{1/2} \tag{9.52a}$$

The solution to equation (9.51b) is

$$f_2 = \left(\frac{K_\beta}{p + K_\beta}\right)^{1/2} \tag{9.52b}$$

while the solution to equation (9.51c) is

$$f_3 = \frac{\left(1 + \frac{8K_\gamma}{p + K_\gamma}\right)^{1/2} - 1}{2} \tag{9.52c}$$

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To provide a smooth and continuous solution, the approximate mol fractions used in equations (9.51), which assume complete decoupling between reactions, are replaced by

$$x_{A_2} = \frac{1 - f_1}{Z} \tag{9.53a}$$

$$x_A = \frac{2(f_1 - f_2)}{Z} \tag{9.53b}$$

$$x_{A+} = \frac{2(f_2 - f_3)}{Z} \tag{9.53c}$$

$$x_{A++} = \frac{2f_3}{Z} \tag{9.53d}$$

$$x_e = \frac{2(f_2 + f_3)}{Z} \tag{9.53e}$$

These mol fractions add to unity as required. With the mol fractions all determined, the equilibrium thermodynamic properties can be calculated readily from the usual summation relations, equations (9.16), (9.17), and (9.18). The specific heats given by equations (9.19) and (9.20) require derivatives of the Zx_i products which are derived from equations (9.52) and (9.53) and lead to relations for df/dT that involve the derivatives $d\ ln\ K/dT$ similar to equations (9.38) and (9.42).

Problem 9.2: Derive expressions for $[\partial(Zx_i)/\partial T]_p$ in terms of the derivatives $(d\ ln\ K_p/dT)$ for the system described by equations (9.51), (9.52), and (9.53). Express the fractions f_1, f_2, and f_3 in terms of concentration standardized equilibrium constants K_c and find the derivatives $[\partial(Zx_i)/\partial T]_\rho$ for the above system in terms of the derivatives $(d\ ln\ K_c/dT)$.

For many problems, trace elements of certain species may be important even though they appear in such small quantity that they do not influence the thermodynamic properties of the gas. For example, rather strong band spectra are observed from N_2^+ even though the concentration may be only a fraction of a percent. The concentration of trace amounts can be estimated if the mol fractions of the major species are assumed to be unchanged. For example, a trace amount of A_2^+ formed according to the chemical balance equation (9.49b) is approximately given by

$$x_{A_2^+} \simeq \frac{{x_A}^2}{x_e} K_\delta \tag{9.54}$$

where x_A and x_e are the major species mol fractions determined above with the decoupled reaction approximation and K_δ is the equilibrium constant given by

$$ln\ K_\delta = -\frac{I-D}{kT} + ln\ Q(A_2^+) + ln\ Q(e) - 2\ ln\ Q(A) \tag{9.55}$$

and I is the ionization energy and D is the dissociation energy of A_2. The mol fraction of A_2^+ could be estimated equally well from other chemical balance equations that involve the molecular ion, such as

$$A_2 \rightleftarrows A_2^+ + e \tag{9.49b'}$$

$$A + A^+ \rightleftarrows A_2^+ \tag{9.49b''}$$

since, as mentioned previously, the equilibrium properties do not depend on the reaction path. However, the reaction (9.49b) tends to be the rate controlling step in the formation of the molecular ion for most diatomic molecules, rather than reactions (9.49b') or (9.49b"). For example, it has a smaller activation energy than (9.49b'), and the lower activation energy process takes greater advantage of the many low energy collisions that occur in gases with Boltzmann kinetic energy distributions. Reaction (9.49b") requires a three-body collision which is less likely than the two-body collision process at usual densities, the third body being required to carry away the excess kinetic energy so that the A_2^+ ion becomes stable.

9.7 DISSOCIATING AND IONIZING NITROGEN

To illustrate the above procedures, the approximate solutions for dissociating and ionizing nitrogen are considered. In addition to the partition functions for N_2 and N given by equations (9.44) and (9.45), the partition functions for N^+, N^{++}, N_2^+, and electrons are required. From known atomic constants (ref. 1), these are approximated as in reference 2:

$$\begin{aligned} \ln Q_p(\mathrm{N}^+) &\approx \frac{5}{2} \ln T + 0.293 \\ &\quad + \ln\left(1 + 3e^{-70.6/T} + 5e^{-188.9/T} + 5e^{-22{,}040/T} + e^{-47{,}030/T} + 5e^{-67{,}870/T}\right) \end{aligned} \tag{9.56}$$

$$\ln Q_p(\mathrm{N}^{++}) \approx \frac{5}{2} \ln T + 0.293 + \ln\left(2 + 4e^{-251.1/T}\right) \tag{9.57}$$

$$\ln Q_p(\mathrm{N}_2^+) \approx \frac{7}{2} \ln T - 0.382 - \ln\left(1 - e^{-3176/T}\right) + \ln\left(2 + 4e^{-13{,}190/T} + 2e^{-36{,}630/T}\right) \tag{9.58}$$

$$\ln Q_p(e) \approx \frac{5}{2} \ln T - 14.236 \tag{9.59}$$

The additional equilibrium constants for single ionization of atoms, double ionization of atoms, and the formation of molecular ions from atomic collisions are

$$\ln K_\beta = -\frac{168{,}840}{T} + \ln Q_p(\mathrm{N}^+) + \ln Q_p(e) - \ln Q_p(\mathrm{N}) \tag{9.60}$$

$$\ln K_\gamma = -\frac{343{,}650}{T} + \ln Q_p(\mathrm{N}^{++}) + \ln Q_p(e) - \ln Q_p(\mathrm{N}^+) \tag{9.61}$$

$$\ln K_\delta = -\frac{67{,}620}{T} + \ln Q_p(\mathrm{N}_2^+) + \ln Q_p(e) - 2\ln Q_p(\mathrm{N}) \tag{9.62}$$

Using these values for the equilibrium constants, one obtains the compressibility shown in figure 9.6 and the enthalpy ratio ZH/RT shown in figure 9.7. The double ionization of atomic nitrogen has very little effect below 15,000° K except at pressures much lower than 10^{-4} atm. Similarly, the ionization of molecular nitrogen is negligible except at pressure much higher than 100 atm. The mol fractions of the different chemical species in equilibrium nitrogen are shown in figure 9.8 for pressures of 1.0 and 10^{-4} atm. For most practical purposes, the electron and N^+

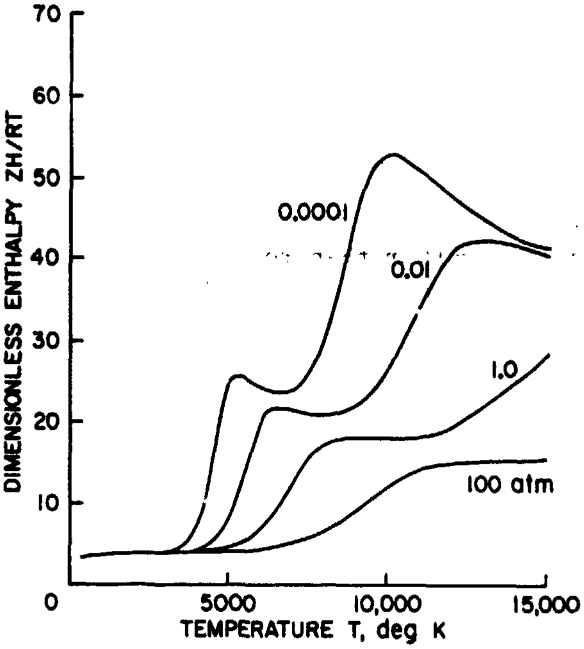
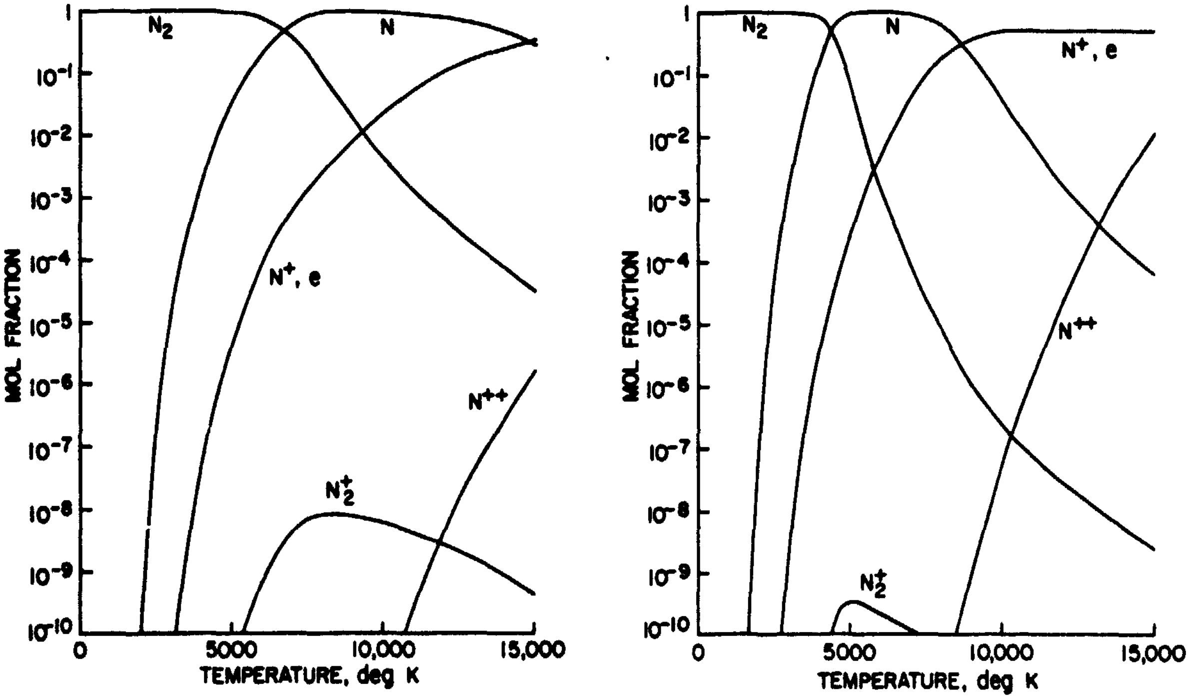


Figure 9.7.- Enthalpy of dissociating, ionizing nitrogen.



(a) 1.0 atm

(b) 0.0001 atm

Figure 9.8.- Equilibrium mol fractions in nitrogen.

mol fractions are equal in this range of T and p, and only small traces of N_2^+ and N^{++} appear. The graphs are similar in appearance; only at higher pressures the dissociation and ionization reactions that increase the total number of particles are delayed until higher temperatures. The production of N_2^+ is also promoted at higher pressure at the expense of the dissociated pair $N + N^+$.

9.8 PROPERTIES OF GAS MIXTURES

In the examples given above, we saw how even a pure gas such as nitrogen becomes a rather complex, chemically reacting mixture at high temperatures, involving four or five principal species and traces of others. A simple gas mixture such as N_2 and O_2 becomes more complex yet. Besides the dissociation and ionization of oxygen, which more or less parallels that of nitrogen, nitric oxide is an important species produced at intermediate temperatures:

$$N_2 + O_2 \rightleftarrows 2NO \tag{9.63}$$

Typically, nitric oxide concentration is a percent or less of the total at normal pressures and lower. It does not greatly influence the thermodynamic properties of the mixture at these levels since the molecular energies are all comparable to those of the O_2 and N_2 species it replaces. However, NO has two very strong radiation bands (the NO β and γ bands) in the violet end of the optical spectrum and is responsible for much of the radiation observed from high-temperature air. More importantly, the ionization energy of NO is rather low, about 9.24 eV, and the major source of electrons in air at moderate temperatures (5,000° to 10,000° K) is NO ionization:

$$NO \rightleftarrows NO^+ + e \tag{9.64}$$

To a first approximation, mol fractions of NO, NO^+, and e can be estimated at pressures of 1 atm or less by the small perturbation method used to find N_2^+ in the preceding example of nitrogen ionization. At higher pressures, these species concentrations must be solved simultaneously with the O_2, N_2, O, N, O_2^+, O^+, N_2^+, and N^+ species concentrations if high accuracy is required. The electrons produced from NO, even though only a very small mol fraction, are sufficient to absorb essentially all the microwave signals beamed through high-temperature air. These electrons are produced in the hot gases about satellite and space vehicles entering the earth's atmosphere, for example, and are responsible for the communications blackout observed during the reentry period of these vehicles. O_2^- and O^- are also important species responsible for scavenging some of the electrons.

In addition to the above species, NO_2, N_2O, and O_3 are formed in trace amounts. Dry air contains traces of CO_2 and A which lead to CO, CO^+, C, C^+, and A^+ in small but noticeable amounts. Normal atmospheric gases also contain sizeable amounts of water vapor, which leads to OH, OH^-, H, H_2, H^+, H^-, CH, and other species. Precise calculations require simultaneous solutions for 30 or 40 species for dry air alone, more for moist air. Relatively precise calculations for dry air have been performed by Hilsenrath and Beckett (ref. 3) and by Gilmore (ref. 4), among others. Calculations done before 1955 were based on a low value for N_2 dissociation and are not accurate. Approximate solutions based on the decoupled reaction method, neglecting the effects of NO, were published by Hansen (ref. 2). Machine calculations of thermodynamic properties were made for hydrogen (refs. 5 and 6), pure CO_2 gas (ref. 7), and CO_2-N_2 mixtures that simulate the Martian atmosphere (ref. 8), among others. With modern, high-speed, digital computers, the complexity of the mixture does not present a severe problem.

Chapter 10 considers some examples of solutions to the flow of gases and to the speed of sound in gases which can be obtained from the equilibrium thermodynamic properties of the gas.

9.9 CONCLUDING REMARKS

Even very simple gas mixtures become a complex mixture of reacting chemical species at high temperature, and precise solutions for the equilibrium properties of such gases require iterative methods on digital computers. However, reasonably good approximate solutions can often be obtained by treating the reactions as independent of one another whenever the characteristic energies of these reactions differ by several electron volts or more. This approximation is particularly good at low pressures or densities where each dissociation and ionization reaction occurs over a relatively narrow temperature span. Then one reaction is completed before the next begins. High-temperature air is an example where this approximation is useful since the characteristic reaction energies are reasonably well spaced: about 0.2 eV for vibrational excitation, 5 eV for O_2 dissociation, 9 eV for N_2 dissociation, 15 eV for single ionization of both N and O, and much higher energies for multiple ionization of the atoms. Such approximate analytic solutions are useful first estimates for precise numerical computer iterative solutions of the equilibrium properties. For air, the production of NO and the ionization of NO are the most important reactions that need to be added to the system.

At high pressures or densities, the uncoupled reaction approximation breaks down because the dissociation and ionization reactions then occur over a relatively broad span of temperature, and the different reactions overlap at pressures of 100 atm and higher in air, for example. Iterative numerical solutions are then required.

As any given reaction runs its course, beginning at low temperature and completing at higher temperature, the energy, enthalpy, and entropy functions are rather suddenly increased, and the specific heats increase to a very high peak. The specific heat at constant volume peaks before the specific heat at constant pressure in any reaction that increases the number of gas particles (such as dissociation or ionization). Then, in this case, any quantity that depends on the ratio of specific heats, such as the Prandtl number, goes through an S-shaped oscillation with both a minimum and a maximum.

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CHAPTER 10 - SOME APPLICATIONS OF EQUILIBRIUM THERMODYNAMIC PROPERTIES TO CONTINUUM GASDYNAMICS

10.1 SUMMARY

The speed of sound for the propagation of isentropic disturbances in a gas is developed, including corrections for chemical reaction. The term "zero frequency" is used to describe this isentropic limit sound speed; the term signifies that changes in the gasdynamic variables are all very slow compared with the chemical rate changes in the gas. A faster, nonisentropic speed of propagation occurs for disturbances where the changes in gasdynamic variables are fast compared with the chemical rate changes. In the limit, this is known as the "infinite frequency" or "frozen" sound speed - the former term calling attention to the very high frequency of the disturbance, the latter term calling attention to the frozen character of the chemical reactions under such rapid changes of state.

The true sound speed for a disturbance of finite frequency is shown to be between these two limits and is expressed in terms of the chemical relaxation time. The Riemann invariants that are useful in determining the changes in flow speed along characteristic directions in supersonic flow are derived in terms of integrations of acoustic impedance, and example results are given for air. Next, solutions for one-dimensional, shock-tube flow produced by the sudden release of a high-pressure reservoir gas into a lower pressure test gas region are derived, first for ideal gas, then for shock waves in a vibrating diatomic gas, and finally for dissociating and ionizing gases. Shock propagation into still gas, shock reflection from a plane end wall, unsteady expansion waves created in the driving reservoir gas, steady expansion waves at an area discontinuity between the reservoir and the shock tube, and interactions between the reflected shock wave and the gas interface between the shocked gas and the expanded reservoir gas are all treated.

10.2 INTRODUCTION

We consider here applications of the thermodynamic properties of real gases, such as developed in the preceding chapters, to a few problems in continuum gasdynamics. First, the speed of sound in the gas is derived and the Riemann invariants used to calculate changes in velocity and other fluid properties along characteristic lines in supersonic flow (ref. 1) are developed. Then the effects of real gases on the properties of gas flows produced in shock tubes are deduced.

10.3 SPEED OF SOUND IN GASES

The speed of sound is, by definition, the speed with which a disturbance of vanishingly small strength propagates through the medium. This speed is generally a function of frequency. When the period of a periodic disturbance is the same order as the characteristic relaxation time of some process in the gas, such as vibrational excitation, dissociation, or ionization, the disturbance wave is dispersed and rapidly attenuates as it propagates through the medium. The characteristic relaxation times of such kinetic processes depend on the temperature and density of the gas, and a very complex relation between sound speed and gas properties ensues. These relations properly follow a study of collision-induced rate processes in gases, but for the present we can examine two limiting cases, knowing only the thermodynamic properties of the gas, namely, completely isentropic flow in which the gas is everywhere in total equilibrium throughout the disturbance wave, and frozen flow in which the kinetic reaction essentially freezes for the period of the disturbance.

Consider first a disturbance with such low frequency that the gas can completely relax to equilibrium conditions throughout the wave, that is, the wave frequency ω is much less than the relaxation time (τ^{-1}) for any process that contributes appreciably to changes in the thermodynamic properties of the gas. Since the disturbance is presumed to be very weak, dissipation terms may be neglected and the flow treated as isentropic:

$$dS = \frac{de + p\,dV}{T} = \frac{de - \frac{p}{\rho^2}\,d\rho}{T} = 0 \qquad (10.1)$$

where e is the specific energy, that is, energy per unit mass. For conservation of total specific enthalpy,

$$de + d\left(\frac{p}{\rho}\right) + a\,da = 0 \qquad (10.2)$$

where a is the velocity of the disturbance through the gas. From equations (10.1) and (10.2), the momentum flux is found to vanish,

$$dp + \rho a\,da = 0 \qquad (10.3)$$

In addition, mass conservation requires that

$$\rho\,da + a\,d\rho = 0 \qquad (10.4)$$

whence

$$a^2 = \left(\frac{dp}{d\rho}\right)_S \qquad (10.5)$$

Equation (10.5) is the basic expression for the velocity with which an isentropic disturbance propagates through a medium. This relation is expressed next in terms of specific heats and derivatives with respect to temperature. Consider e as a function of p and ρ with equation (10.1):

$$\left(\frac{de}{d\rho}\right)_S = \left(\frac{de}{dp}\right)_\rho \left(\frac{dp}{d\rho}\right)_S + \left(\frac{de}{d\rho}\right)_p = \frac{p}{\rho^2} \tag{10.6}$$

The derivative $(de/dp)_\rho$ can be expressed as

$$\left(\frac{de}{dp}\right)_\rho = \left(\frac{de}{dT}\right)_\rho \left(\frac{dT}{dp}\right)_\rho = C_v \left(\frac{dT}{dp}\right)_\rho \tag{10.7}$$

Then, from equations (10.6) and (10.7),

$$C_v \left(\frac{dp}{d\rho}\right)_S = \frac{p}{\rho^2} \left(\frac{dp}{dT}\right)_\rho - \left(\frac{de}{d\rho}\right)_p \left(\frac{dp}{dT}\right)_\rho \tag{10.8}$$

According to a well-known theorem about partial derivatives of implicit functions of three variables (ref. 2),

$$\left(\frac{dp}{d\rho}\right)_T \left(\frac{d\rho}{dT}\right)_p \left(\frac{dT}{dp}\right)_\rho = -1 \tag{10.9}$$

Thus

$$\begin{aligned}
C_v \left(\frac{dp}{d\rho}\right)_S &= -\frac{p}{\rho^2} \left(\frac{dp}{d\rho}\right)_T \left(\frac{d\rho}{dT}\right)_p - \left(\frac{de}{dT}\right)_p \left(\frac{dT}{d\rho}\right)_p \left(\frac{dp}{dT}\right)_\rho \\
&= \left(\frac{dp}{d\rho}\right)_T \left[\left(\frac{de}{dT}\right)_p - \frac{p}{\rho^2} \left(\frac{d\rho}{dT}\right)_p\right] \\
&= \left(\frac{dp}{d\rho}\right)_T \left[\frac{d}{dT}\left(e + \frac{p}{\rho}\right)\right]_p = C_p \left(\frac{dp}{d\rho}\right)_T
\end{aligned} \tag{10.10}$$

Now, from equations (10.5) and (10.10),

$$a^2 = \left(\frac{dp}{d\rho}\right)_S = \frac{C_p}{C_v} \left(\frac{dp}{d\rho}\right)_T = -\gamma \frac{\left(\frac{dp}{dT}\right)_\rho}{\left(\frac{d\rho}{dT}\right)_p} \tag{10.11}$$

a perfectly general relation regardless of the state of the gas, if the disturbance is isentropic. If the equation of state is expressed in terms of the compressibility Z,

$$\frac{p}{\rho} = Z\left(\frac{R}{M_O}\right)T \tag{10.12}$$

the square of the speed of sound can be expressed as

$$a^2 = \gamma \frac{p}{\rho}\left[\frac{1 + T\left(\frac{d\ ln\ Z}{dT}\right)_\rho}{1 + T\left(\frac{d\ ln\ Z}{dT}\right)_p}\right] \tag{10.13}$$

This is the usual relation for ideal gases except for the correction term in brackets. This correction term is slightly less than unity for dissociating and ionizing gases, according to the law of mass action. As T increases at constant ρ, p increases, and while Z also increases, the increase in Z is inhibited by the increase in pressure. Thus Z does not increase as rapidly at constant density as it would at constant pressure:

$$\left(\frac{d\ ln\ Z}{dT}\right)_\rho < \left(\frac{d\ ln\ Z}{dT}\right)_p \tag{10.14}$$

The correction factor is unity for any gas where Z is constant, that is, where the reactions that occur in the medium do not change the number of gas particles.

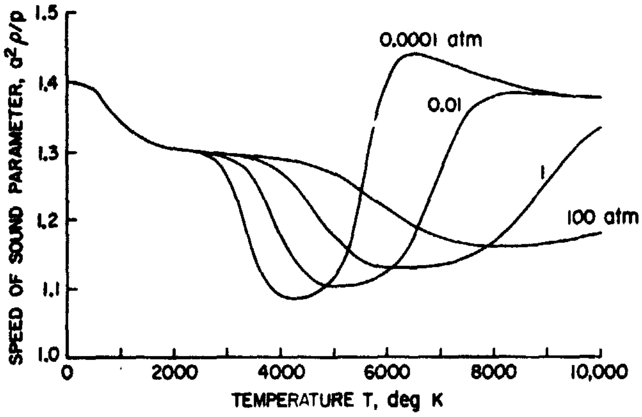


Figure 10.1.- Speed of sound parameter for vibrating, dissociating nitrogen (ionization reactions frozen).

The speed-of-sound parameter $(a^2\rho/p)$ is shown as a function of temperature at various pressures in figure 10.1 for dissociating nitrogen, neglecting the ionization reactions.

For very high frequency, the chemical reactions cannot follow the rapid changes in pressure and temperature produced by the disturbance wave, and the reactions are said to be frozen. Then

$$a^2 = \gamma_f \frac{p}{\rho} \tag{10.15}$$

which is the same as the ideal gas relation except that the ratio of specific heats γ_f must include only those internal degrees of freedom in equilibrium with the kinetic energy. For a gas mixture with mol fractions x_i,

$$\gamma_f = \frac{\sum_i x_i \left(\frac{C_p}{R}\right)_i}{\sum_i x_i \left(\frac{C_v}{R}\right)_i} \tag{10.16}$$

$$\left(\frac{C_p}{R}\right)_i = \frac{n_i + 5}{2} \tag{10.17}$$

$$\left(\frac{C_v}{R}\right)_i = \frac{n_i + 3}{2} \tag{10.18}$$

where n_i is the number of internal degrees of freedom of the component i in equilibrium with the kinetic energy. For atomic particles and electrons, $n_i = 0$. For diatomic particles, the rotational energy is normally in full equilibrium with the kinetic energy and $n_i = 2$. For nonlinear polyatomic molecules, three rotational modes are present and $n_i = 3$. Vibrations, on the other hand, normally require a large collision number Z_c, of the order of 10^3 - 10^6, before they become fully excited. If the frequency is greater than θ_c/Z_c, where θ_c is the collision rate, the vibrational modes are frozen. (Note that the gas is essentially opaque to frequencies greater than θ_c, and disturbances do not propagate effectively in this case.) At frequencies much less than θ_c/Z_c, vibrations are also excited. Then, for diatomic particles, $n_i = 4$; for linear triatomic particles, $n_i = 10$; and for nonlinear triatomic particles, $n_i = 9$. At very high temperature (high collision velocities), Z_c approaches unity, and the internal degrees of freedom tend to remain in equilibrium with kinetic energy even at very high frequencies. At very low density, the collision rate becomes small and only low-frequency waves propagate through the gas.

In accord with the above, at normal temperatures in a diatomic gas, $\gamma_f = 7/5$. At temperatures where dissociation barely starts, the vibrational relaxation is typically very fast and $\gamma_f \to 9/7$. When dissociation is complete, $\gamma_f \to 5/3$.

Where a rate process occurs in the gas with a characteristic relaxation time τ of the order of the reciprocal frequency ω^{-1}, disturbance waves propagate through the medium with a speed between the frozen speed a_f and the equilibrium speed a_e:

$$a_e < a < a_f \tag{10.19}$$

The amplitude, $v(x)$, of a disturbance represented by the function $u(x,t) = v(x)e^{i\omega t}$ is the solution to the wave equation (ref. 3)

$$\frac{d^2v}{dx^2} + \left(\frac{\omega}{a_f}\right)^2 \left[\frac{\left(\frac{a_f}{a_e}\right)^2 + i\omega\tau}{1 + i\omega\tau}\right] v = 0 \tag{10.20}$$

which is a damped sine wave with the speed

$$a = a_f \left[\frac{1 + (\omega\tau)^2}{\left(\frac{a_f}{a_e}\right)^4 + (\omega\tau)^2}\right]^{1/4} \tag{10.21}$$

The wave is damped by the exponential factor

$$exp\left[- \frac{(a_f/a_e)^2 - 1}{(a_f/a_e)^2 + (\omega\tau)^2} \frac{\omega^2\tau x}{2a}\right] \tag{10.22}$$

When ω or τ vanishes, $a \to a_e$ and the damping is negligible. On the other hand, when $\omega\tau$ becomes very large, $a \to a_f$ and damping also becomes large with an absorption path $2a_f\tau/[(a_f/a_e)^2 - 1]$.

10.4 RIEMANN INVARIANTS

The change in velocity of an isentropic flow along the characteristic directions in supersonic flow is given by (ref. 1)

$$u - u_i = \pm(l_i - l) \tag{10.23}$$

where subscript i refers to initial conditions and l is the reciprocal acoustic impedance $(\rho a)^{-1}$ (i.e., the acoustic admittance) integrated with respect to pressure:

$$l = \int_{p_o}^{p} \frac{dp}{\rho a} = \int_{\rho_o}^{\rho} \frac{a\ d\rho}{\rho} \tag{10.24}$$

The positive sign in equation (10.23) corresponds to changes along the positive characteristic in the time-distance (x,t) plane:

$$\frac{dx}{dt} = u + a \tag{10.25a}$$

where u is the flow velocity; the negative sign corresponds to changes along the negative characteristic,

$$\frac{dx}{dt} = u - a \tag{10.25b}$$

Equations (10.24) and (10.25) determine all the changes of gas properties in one-dimensional isentropic flow, through the dependence of velocity on pressure. Since only differences of the quantity l are required, the lower limit of the integral in equation (10.24), p_o, is arbitrary. Typically, p_o is taken to equal zero so that l will always be positive. The so-called Riemann invariants of the flow, r and s, are given by the sum and difference relations:

$$u + l = 2r \tag{10.26a}$$

$$u - l = -2s \tag{10.26b}$$

Once these are established at any point (x_i, t_i) in the flow with known conditions, the remaining flow in the x,t plane may be calculated, provided the flow is isentropic, that is, shock free.

At low temperatures where the gas behaves ideally, the isentropic relation between pressure and density is

$$p = \left(\frac{p_o}{\rho_o{}^{\gamma}}\right) \rho^{\gamma} \tag{10.27}$$

and the speed of sound can be expressed as

$$a^2 = \left(\frac{dp}{d\rho}\right)_S = \left(\gamma \frac{p_o}{\rho_o{}^{\gamma}}\right) \rho^{\gamma - 1} = \gamma \frac{p}{\rho} \tag{10.28}$$

The quantity l is then given by

$$l = \int_o^{\rho} \frac{a\, d\rho}{\rho} = \left(\gamma \frac{p_o}{\rho_o{}^{\gamma}}\right)^{1/2} \int_o^{\rho} \rho^{(\gamma - 3)/2}\, d\rho = \frac{2}{\gamma - 1}\, a \tag{10.29}$$

where $\rho_o = 0$ has been chosen as the reference level.

The quantity l/l^* for air is calculated in figure 10.2 for zero frequency, where the speed of sound is the equilibrium value given by equation (10.17). The quantity l^* is the ideal gas value given by equation (10.29) where $\gamma = 1.4$ and $a = (\gamma RT)^{1/2}$. The effects of vibration, dissociation, and single ionization of the air particles are included, but the NO formation reaction was omitted for convenience in calculation. Details of the calculation may be found in reference 4. The ratio l/l^* is shown for constant entropy values ZS/R of 30, 40, 50, 60, and 70 and for constant pressure values of 10^{-4}, 10^{-2}, 10^{0}. and 10^{2} atm.

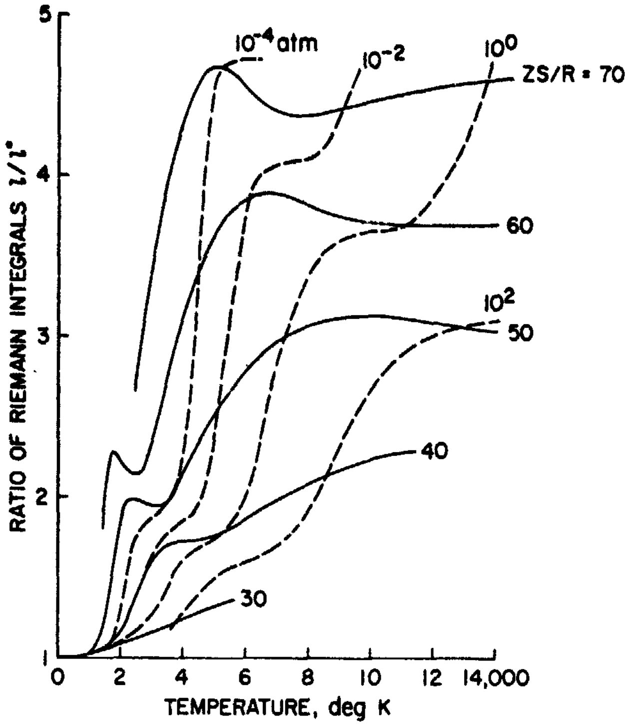


Figure 10.2.- Riemann integral for air compared with ideal gas values for constant specific entropy.

The utility of the integral l in one-dimensional flow problems results from the fact that it is a function only of local gas properties; thus l need be computed only once for any given entropy and pressure (or density or temperature) and tabulated or graphed as in figure 10.2. For two- or three-dimensional flow, the relations between changes in flow properties depend not only on local gas properties, but on the initial or stagnation conditions as well. For example, the change in Prandtl-Meyer expansion angle may be expressed as

$$\nu_2 - \nu_1 = \int_{u_1}^{u_2} \left(\frac{u_2}{a^2} - 1\right)^{1/2} \frac{du}{u} \qquad (10.30)$$

where the integral is performed along a constant isentrope. The limits of the integral are functions of the local enthalpy per unit mass h_i and the stagnation enthalpy h_t:

$$\frac{u_i^2}{2} = h_t - h_i \qquad (10.31)$$

Thus, in this case, a third dimension must be added to the table of the Prandtl-Meyer angle for real gas expansions, which would specify the stagnation conditions.

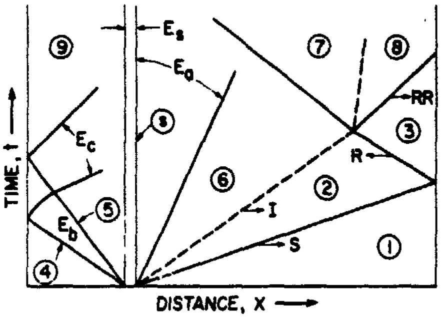
With this introduction to the effects of real gas on the speed of sound and derivative quantities in mind, next consider the flow of real gases in shock tubes.

10.5 SHOCK-TUBE FLOW

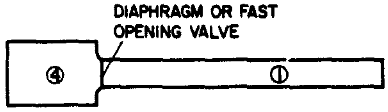
The shock tube is a well-known device used to produce uniform samples of gas at precisely known temperatures and pressures for a limited time duration. The situation is idealized here by neglecting the effects of boundary-layer flow and assuming that the flow is one-dimensional throughout. These idealizations are realistic if the shock tube is not too long (length diameter ratio of the order of 100 or less) and if the gas pressure is not loo low (the order of 10^{-4} atm or higher).

The mathematical theory of shock waves and expansion waves is elegantly treated by Courant and Friedrichs (ref. 1). Glass and Patterson (ref. 5) give a good summary of the shock-tube relations for ideal gases, and a detailed account of the mathematical derivations for ideal gas, shock-tube flow is given in reference 6. When gases do not obey the ideal gas law, such as dissociating and ionizing gases, the shock-tube relations cannot be given analytically in terms of initial conditions, but must be obtained by iterative procedures. Brief outlines of these procedures are presented by Romig (ref. 7) and Feldman (ref. 8).

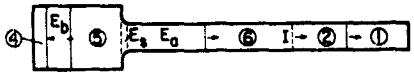
The shock tube involves a number of distinct flow regions, as shown in the time-distance diagram in figure 10.3(a). The initial condition of the shock tube, with a high-pressure reservoir (region 4), a low-pressure test region (region 1), and a diaphragm or quick-acting valve separating the two regions is diagrammed in figure 10.3(b). A short time after the diaphragm is ruptured, or the valve opened, a shock wave forms and travels down the tube, followed by the expanding high-pressure driver gas, (fig. 10.3(c)). The contact between the test gas and the driver gas is shown as a surface, but in high-energy shock tubes this is typically a mixing zone of finite width. The expansion wave originating at the diaphragm may consist of both an unsteady expansion E_a that accelerates the driven gas to the proper velocity in the one-dimensional channel and a steady-state expansion E_s to match the flow velocities across the step in area ratios from driver chamber to test chamber. An unsteady expansion E_b also feeds back into the driver chamber to equalize the pressures involved.



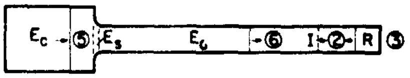
(a) Time-distance diagram.



(b) Initial condition.



(c) Incident shock propagates down tube after diaphragm burst.



(d) Shock reflected from end wall propagates back into tube.

Figure 10.3.- Shock-tube flow.

The gas compressed by the shock wave (region 2) is elevated in temperature and pressure to values uniquely related to the shock velocity, an easily measured quantity. This gas is often used as a test specimen. The test duration - the time interval between the appearance of the shock and the contact region at the test station - typically varies from the order of a millisecond at moderate shock speeds to microseconds at very high shock speeds. The driver gas may be of low molecular weight, such as He, to obtain higher shock velocities and higher test gas temperature for a given pressure. The driver gas may also be heated to provide stronger shocks. Typically, however, higher temperature test gas is obtained by reflecting the shock from the end wall of the tube. This situation is diagrammed in figure 10.3(d). The test duration then is the interval between the reflection of the shock from the end wall and the appearance of shock waves or expansion waves reflected from the contact surface, or the expansion waves feeding forward from the diaphragm position or the end of the driver chamber, whichever appears first. Again, the gas properties are uniquely related to the shock velocity.

Because of the number of different regions involved and of the relations between flow quantities required, a following list of symbols used in the analysis will prove helpful, particularly since some of these symbols duplicate symbols used previously with different meanings.

a	speed of sound, $\sqrt{(dp/d\rho)_S}$
A	cross-sectional area
B	$(\rho_{21} - 1)(1 - p_{12})$
C_p	specific heat at constant pressure
C_v	specific heat at constant density
E	expansion wave
h	enthalpy per unit mass, also Planck's constant
I	interface between test and driver gas
k	Boltzmann constant
M	Mach number, ratio of flow speed to speed of sound
p	pressure
R	gas constant, also reflected shock
S	entropy, also incident shock
t	time
T	temperature
u	velocity of gas relative to incident shock
v	velocity of gas relative to shock tube
V	velocity of incident shock relative to shock tube
W	velocity of gas relative to reflected shock
α	$\frac{2h\rho}{p} - 1$; for ideal gas, $\alpha = \frac{\gamma + 1}{\gamma - 1}$

γ	ratio of specific heats, $\frac{C_p}{C_v}$
θ	vibrational constant, $\frac{h\nu}{k}$
ν	vibrational frequency
ρ	density

Superscripts

*	value of property for ideal gas, $\gamma = 1.4$
o	stagnation condition

Subscripts

0	standard conditions of T and p, also conditions on high-pressure side of an expansion wave
1	initial conditions in shock tube
2	condition following normal shock S
3	condition following reflected shock R
4	initial conditions in reservoir
5	reservoir conditions following unsteady expansion wave E_b
6	conditions following gas interface I but preceding unsteady expansion E_a
7	conditions following the reflected wave R after it passes through interface I
8	conditions following the reflected wave RR formed by interaction of shock R with interface I (RR may be an expansion or a compression wave, depending on conditions in region 6)
9	conditions after reflection of expansion wave E_b from end of reservoir
$x_{ik} = x_i/x_k$ $x_{ki} = x_k/x_i$	ratios of quantities designated by a double subscript notation

10.6 SHOCK WAVES

Shocks are commonly treated as discontinuities in the gas properties, whereas the shock actually may encompass a finite region in which nonisentropic rate processes occur, the total reaction zone propagating through the medium at supersonic velocity. This region may be a few millionths of a centimeter thick or it may span many light years, as in a collision between stellar gas clouds. Equilibrium may be reached in a few mean free paths, as in the weak waves produced in normal air, or many billions of collisions may be required to reach equilibrium where chemical processes are involved. Regardless of the processes occurring within the shock and the structure and dimensions of the shock, the equations of continuity determine the relations between properties on either side of the shock region.

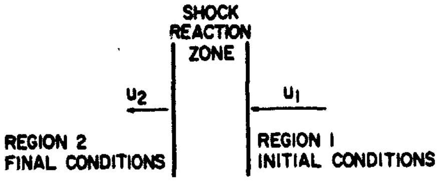


Figure 10.4.- Normal shock wave.

Consider the normal shock region shown in figure 10.4. Gas enters the shock with velocity u_1 and leaves with velocity u_2. If the shock is propagating with the velocity V into a gas at rest,

$$v_1 = 0 , \quad V = -u_1 \tag{10.32}$$

and the velocity of the gas behind the shock wave relative to the stationary reference system is

$$v_2 = -(u_1 - u_2) \tag{10.33}$$

The shock region is defined so that steady-state conditions are attained in region 2. However, the steady-state may be either a true equilibrium condition or a quasi-equilibrium condition in which certain modes of energy in the gas are frozen or essentially uncoupled from the kinetic energy modes during the time scale of interest (which may be the order of milliseconds for the shock tube, but the order of years for interstellar shock-wave phenomena). Either way, the continuity of mass, momentum flux, and energy must be satisfied across the shock region

$$\rho_1 u_1 = \rho_2 u_2 \tag{10.34}$$

$$\rho_1 u_1^2 + p_1 = \rho_2 u_2^2 + p_2 \tag{10.35}$$

$$h_1 + \frac{u_1^2}{2} = h_2 + \frac{u_2^2}{2} \tag{10.36}$$

Elimination of u_2 from equations (10.34) and (10.35) gives

$$u_1^2 = \frac{p_1}{\rho_1}\frac{p_{21} - 1}{1 - \rho_{12}} \tag{10.37}$$

Combination of equations (10.33), and (10.34), and (10.37) yields

$$v_2^2 = (u_1 - u_2)^2 = \frac{p_1}{\rho_1}(p_{21} - 1)(1 - \rho_{12}) \tag{10.38}$$

and, from equations (10.34), (10.36), and (10.37),

$$(p_{21} - 1)(\rho_{12} + 1) = (\alpha_1 + 1)(h_{21} - 1) \tag{10.39}$$

where $(\alpha_1 + 1)$ is the dimensionless parameter $(2h_1\rho_1/p_1)$. Note that the shock relations given by equations (10.37), (10.38), and (10.39) are valid for all steady-state shocks regardless of the equation of state of the gas or of the processes that occur in the shock region. Equation (10.39) is the fundamental shock-wave relation between three variables p_{21}, ρ_{21}, and h_{21}, any one of which may be chosen as the independent variable. Then solutions for the remaining two can be obtained with the aid of the additional relation given by the equation of state of the gas:

$$\rho = \rho(p,h) \tag{10.40}$$

Shock waves need not be normal to the flow, of course. A velocity component tangential to the shock surfaces may exist and the shock then lies obliquely to flow. The tangential component is merely conserved, and a simple transformation to a coordinate system moving at this tangential velocity leaves the normal shock relations given above.

10.7 IDEAL GAS SHOCK RELATIONS

For an ideal gas, the quantity α is a constant:

$$(\alpha + 1) = \frac{2\rho h}{p} = \frac{2\gamma}{\gamma - 1} \tag{10.41}$$

so that

$$p_{21} = \rho_{21}h_{21} \tag{10.40a}$$

Choose p_{21} as the independent variable and solve for h_{21} and ρ_{21} from equations (10.39) and (10.40a) to obtain

$$h_{21} = \frac{p_{21} + \alpha}{\alpha p_{21} + 1}p_{21} \tag{10.42}$$

$$\rho_{21} = \frac{\alpha p_{21} + 1}{p_{21} + \alpha} \qquad (10.43)$$

Note that for very strong shock waves the enthalpy ratio approaches a simple function of pressure

$$h_{21} \xrightarrow[p_{21}>>1]{} \frac{p_{21}}{\alpha} \qquad (10.42a)$$

and the density ratio approaches a constant limit

$$\rho_{21} \xrightarrow[p_{21}>>1]{} \alpha \qquad (10.43a)$$

The limit $\alpha = 6$ obtains for air and other diatomic gases with rotations fully excited but vibrations frozen. For monatomic gases such as He, $\alpha = 4$.

Problem 10.1: Transform the independent variable to the shock Mach number (ratio of shock speed to speed of sound):

$$M = \frac{u_1}{a_1} = \frac{u_1}{(\gamma p_1/\rho_1)^{1/2}}$$

and show that the shock relations reduce to

$$p_{21} = \frac{2\gamma M^2 - (\gamma - 1)}{\gamma + 1}$$

$$\rho_{21} = \frac{(\gamma + 1)M^2}{(\gamma - 1)M^2 + 2}$$

$$h_{21} = \frac{[2\gamma M^2 - (\gamma - 1)][(\gamma - 1)M^2 + 2]}{(\gamma + 1)^2 M^2}$$

Consider next the shock reflected from a fixed wall at the end of the shock tube as shown in figure 10.5, again for ideal gas. Let W be the velocity of the gas relative to the reflected shock R. The relations between properties across the reflected shock are the same as for the incident shock. Equations (10.37), (10.38), and (10.39) are all valid with subscript 2 replacing 1 and subscript 3 replacing 2; for the ideal gas, equations (10.42) and (10.43) are satisfied in the same way.

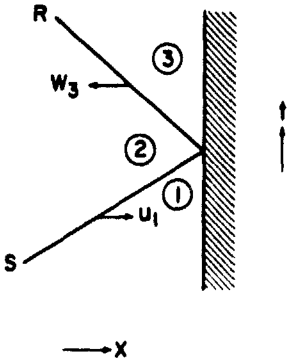


Figure 10.5.- Shock reflection from a fixed wall.

The fixed-wall boundary imposes the condition that the velocity of the gas in region 3 is zero ($v_3 = 0$), so the velocity of the reflected shock is just the velocity with which the gas leaves the reflected shock, W_3. The velocity with which the gas enters the reflected shock is thus

$$W_2 = v_2 + W_3 \qquad (10.44)$$

and from equation (10.38),

$$(W_2 - W_3)^2 = (u_1 - u_2)^2 = \frac{p_1}{\rho_1}(p_{21} - 1)(1 - \rho_{12}) = \frac{p_2}{\rho_2}(p_{32} - 1)(1 - \rho_{23}) \qquad (10.45)$$

Including the equation of state, there are three equations specified that may be solved for the three unknowns p_{32}, ρ_{32}, and h_{32}:

$$(p_{32} - 1)(1 + \rho_{23}) = (h_{32} - 1)(\alpha_2 + 1) \qquad (10.46a)$$

$$(p_{21} - 1)(1 - \rho_{12}) = p_{21}\rho_{12}(p_{32} - 1)(1 - \rho_{23}) \qquad (10.46b)$$

$$p_{32} = f(\rho_{23}, h_{32}) \qquad (10.46c)$$

These equations are still perfectly general for imperfect gas as well as perfect gas. For the ideal gas, α is constant and

$$p_{32} = \frac{h_{32}}{\rho_{23}} \qquad (10.40b)$$

In this case, equations (10.46) can be reduced to

$$\frac{(p_{21} - 1)^2}{\alpha + p_{21}} = p_{21}\frac{(p_{32} - 1)^2}{\alpha p_{32} + 1} \qquad (10.47)$$

for which a solution is

$$p_{32} = \frac{(\alpha + 2)p_{21} - 1}{\alpha + p_{21}} \qquad (10.48)$$

The remaining properties in region 3 can be calculated once p_{32} is known, of course.

10.8 SHOCK WAVES IN VIBRATING DIATOMIC GAS

The simplest type of non-ideality is encountered when specific heat is not constant but the ideal gas law is obeyed. This occurs, for example, at temperatures where diatomic molecules are set into vibration but are not dissociated. The enthalpy of the diatomic molecule gas is given in terms of the characteristic vibrational temperature $\theta = h\nu/k$ as

$$h = \frac{5}{2}\frac{RT}{M} + \frac{R\theta}{M}\left(e^{\theta/T} - 1\right)^{-1} \tag{10.49}$$

Consider only the case where the initial temperature is so low ($T_1 << \theta$) that vibrations are not excited in region 1. Then the initial enthalpy is just $5RT_1/2M$ and the enthalpy ratio across the shock is

$$h_{21} = T_{21} + \frac{2\theta}{5T_1}\left(e^{\theta/T_2} - 1\right)^{-1} \tag{10.50}$$

From the ideal gas equation of state,

$$\rho_{12} = \frac{T_{21}}{p_{21}} \tag{10.51}$$

and the basic shock-wave equation for $\alpha = 6$ is

$$(p_{21} - 1)(\rho_{12} + 1) = 7(h_{21} - 1) \tag{10.52}$$

A quadratic relation for p_{21} in terms of T_{21} results:

$$p_{21}^2 + [(T_{21} + 6) - 7h_{21}]p_{21} - T_{21} = 0 \tag{10.53}$$

which may be solved for p_{21} once T_1 and T_{21} are chosen. The values of p_{21} and T_{21} then determine all other quantities in region 2.

For air, the oxygen and nitrogen molecules have different vibrational frequencies

$$\theta(O_2) = 2270° \text{ K}\ , \qquad \theta(N_2) = 3390° \text{ K} \tag{10.54}$$

At $T_1 = 293°$ K, the enthalpy ratio across a shock wave in air is given by

$$h_{21} = T_{21} + 0.62\left(e^{7.75/T_{21}} - 1\right)^{-1} + 3.70\left(e^{11.56/T_{21}} - 1\right)^{-1} \tag{10.55}$$

and the pressure ratio is

$$p_{21} = \frac{(7h_{21} - T_{21} - 6) + \sqrt{(7h_{21} - T_{21} - 6)^2 + 4T_{21}}}{2} \tag{10.56}$$

Since conditions in regions 1 and 2 determine the strength of the reflected shock, one cannot treat this quantity as an independent variable, and the solutions for region 3 must be found by iteration. Rearrange equation (10.45) to

$$(p_{32} - 1)(1 - \rho_{23}) = B_2 \tag{10.57}$$

where $B_2 = (u_1 - u_2)^2(\rho_1/p_1)(\rho_{21}/p_{21})$ or $(\rho_{21} - 1)(1 - p_{12})$. The basic shock equation for the reflected wave is (see eq. (10.39))

$$(p_{32} - 1)(1 + \rho_{23}) = (\alpha_2 + 1)(h_{32} - 1) \tag{10.58}$$

where $(\alpha_2 + 1) = (\alpha_1 + 1)(h_{21}\rho_{21}/p_{21})$. The enthalpy ratio is a function of the temperature ratio

$$h_{32} = \frac{h_{31}}{h_{21}} \tag{10.59}$$

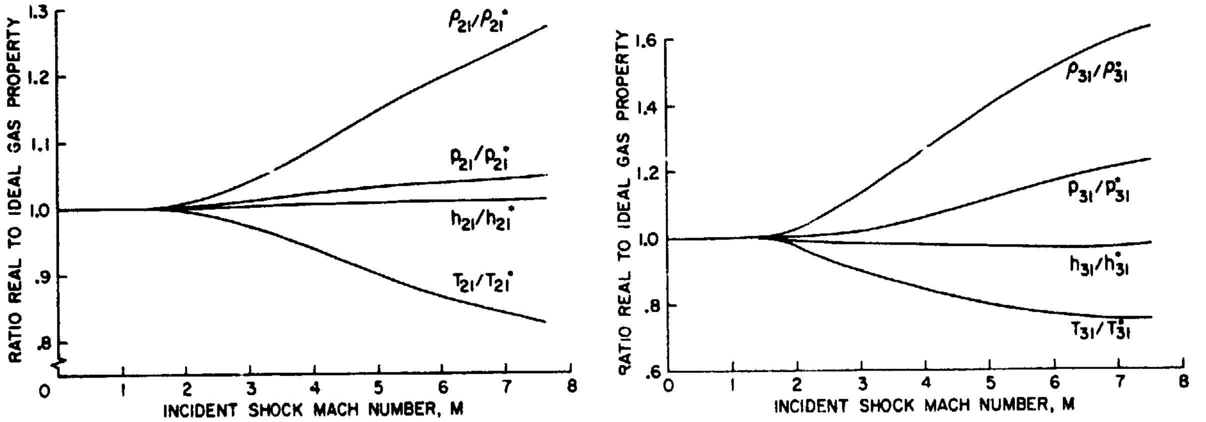
where h_{31} is given by equation (10.55) with subscript 3 replacing 2. The ideal gas law

$$\rho_{23} = \frac{T_{32}}{p_{32}} \tag{10.60}$$

provides the additional relation needed to solve the set of simultaneous equations (10.57) through (10.60). The first, second, and fourth equations of this set can be put into the form

$$p_{32} = T_{32}\,\frac{(\alpha_2 + 1)(h_{32} - 1) + B_2}{(\alpha_2 + 1)(h_{32} - 1) - B_2} \tag{10.61}$$

Several different iteration procedures are possible. One procedure is to choose T_{32}, calculate p_{32} from equation (10.61), and determine whether equation (10.57) is satisfied. If not, repeat the choice of T_{32} until equation (10.57) is satisfied. Some results for shock waves in air with the initial temperature $T_1 = 293°$ K are given in figure 10.6.



(a) Incident shock properties. (b) Reflected shock properties.

Figure 10.6.- Shock relations in air with vibrational effects included (T = 293° K, dissociation and ionization reactions frozen).

10.9 SHOCK WAVES IN DISSOCIATING AND IONIZING GASES

Where the gas dissociates or ionizes, the ideal gas equation of state is no longer obeyed and the entire solution must be found by iteration. This is readily accomplished with digital computers, but a semigraphical procedure is outlined to better illustrate the relationships involved. The real gas effects are conveniently accounted for with a plot of $(C_p/R)_o(p/\rho h)$ or $(p/p_o)/(\rho/\rho_o)(h/h_o)$, as a function of h/h_o. Subscript o refers to a standard state, here taken as 1 atm of pressure and 273° K. The normalizing parameter $(C_p/R)_o$ is the ratio of specific heat to the gas constant evaluated at the standard condition:

$$\left(\frac{C_p}{R}\right)_o = \frac{\rho_o h_o}{p_o} = \frac{\gamma}{\gamma - 1} \tag{10.62}$$

The quantity $(C_p/R)_o(p/\rho h) = 1$ for the ideal gas and falls below unity as the gas molecules begin to vibrate, dissociate, and ionize.

The advantage gained from plotting a normalized parameter such as $(C_p/R)_o(p/\rho h)$ rather than the state variables directly is that a wide range of conditions can be put on a single plot which can be read with nearly uniform accuracy over the entire range of variables. Also, it is relatively easy to interpolate with good accuracy. These advantages are retained when a digital machine is used to interpolate between stored tabulations. For example, figure 10.7 is a set of curves plotted from Hilsenrath and Beckett's data for air (ref. 9).

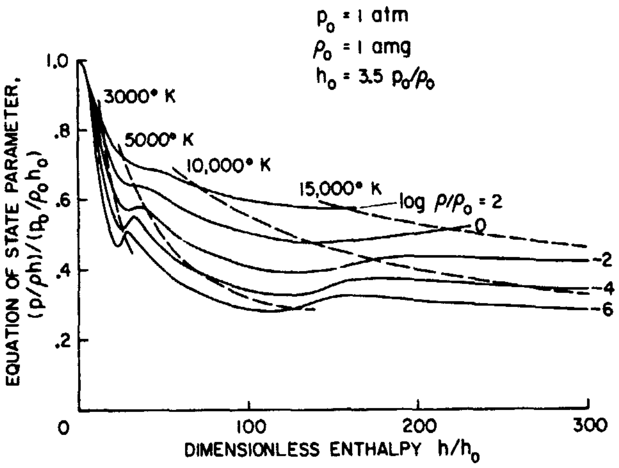


Figure 10.7.- Normalized equation of state parameter $p/\rho h$ for equilibrium air as a function of normalized enthalpy.

As usual, a variety of iteration schemes leading to a solution is possible. One method is as follows:

(1) Specify the initial conditions p_1, ρ_1, and h_1 and the enthalpy ratio h_{21}; calculate h_2.

(2) Choose the density ratio ρ_{21} and calculate ρ_2.

(3) From the graph in figure 10.7, find $(C_p/R)_o(p/\rho h)_2$ for the given h_2 and ρ_2, then calculate p_2 and p_{21}.

(4) Determine whether the basic shock relation equation (10.39) is satisfied.

(5) If not, start at step 2 with a new choice of ρ_{21} and repeat until the equality, step 4, is satisfied.

The density ratio ρ_{21} is a relatively slowly varying quantity so one can easily choose a value close to solution. The iterations generally converge to a solution better than 1 percent in three or four tries. If the results are plotted as a function of shock-wave Mach number, the results are not very sensitive to small differences in initial conditions.

The quantity B_2 used in equation (10.57) is needed for the reflected-shock calculations and is given by

$$B_2 = \frac{(p_{21} - 1)(1 - \rho_{12})}{p_{21}\rho_{12}} \tag{10.63}$$

Eliminate ρ_{23} from equations (10.57) and (10.58) to obtain

$$2(p_{32} - 1) = B_2 + (\alpha_2 + 1)(h_{32} - 1) \tag{10.64}$$

The density ratio is then

$$\rho_{23} = 1 - \frac{B_2}{p_{32} - 1} \tag{10.65}$$

One iterative scheme for calculating reflected-shock properties is

(1) Choose the ratio h_{32}.

(2) Calculate p_{32} from equation (10.64) and ρ_{23} from equation (10.65).

(3) Calculate ρ_3, h_3, and p_3.

(4) From the graph in figure 10.7, select the value of $(C_p/R)_o(p/h\rho)_3$ that corresponds to the values ρ_3 and h_3 found in step 3.

(5) Determine whether $(C_p/R)_o(p/h\rho)_3 = (3.5p_3)/(\rho_3 h_3)$.

(6) If not, start at step 1 with a new choice of h_{32} and repeat until the equality in step 5 is satisfied.

By definition, W_3 is the velocity with which the gas recedes from the reflected shock in region 3; it is also the velocity of the reflected shock due to the fixed boundary condition at the wall. From mass continuity,

$$\rho_2(|v_2| + W_3) = \rho_3 W_3 \tag{10.66}$$

while from equation (10.34) and the definition of v_2,

$$|v_2| = |u_1|(1 - \rho_{12}) \tag{10.67}$$

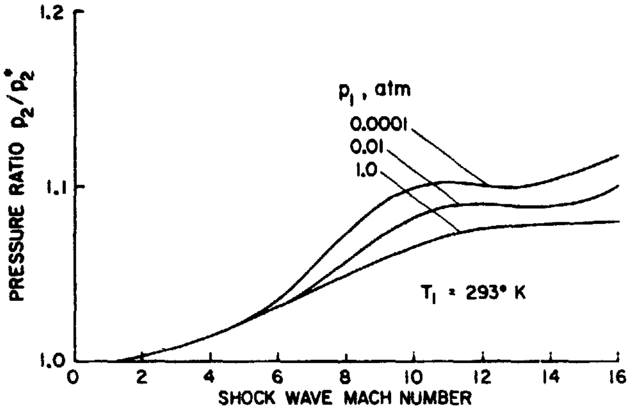
Thus the ratio of the reflected-shock speed to the incident shock speed is

$$\frac{W_3}{|u_1|} = \frac{1 - \rho_{12}}{\rho_{32} - 1} \tag{10.68}$$

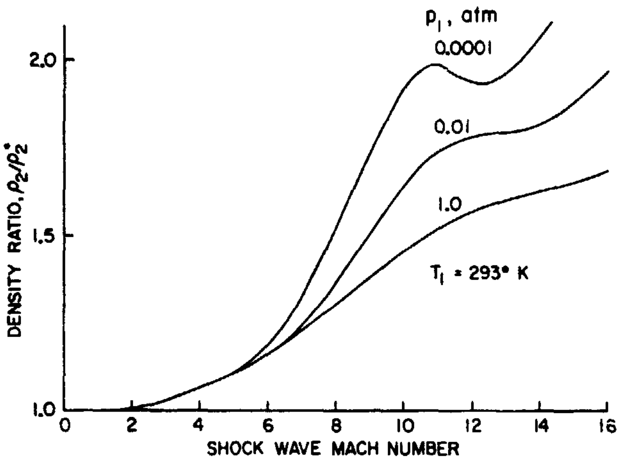
The reflected shock meets the interface at a distance $\rho_{13}L$ from the end of the shock tube, where L is the length of the tube. The time interval between the reflection of the shock and the interaction with the interface is thus

$$\Delta t = \frac{\rho_{13}L}{W_3} = \frac{\rho_{13}(\rho_{32} - 1)}{1 - \rho_{12}} \frac{L}{M_1 a_1} \tag{10.69}$$

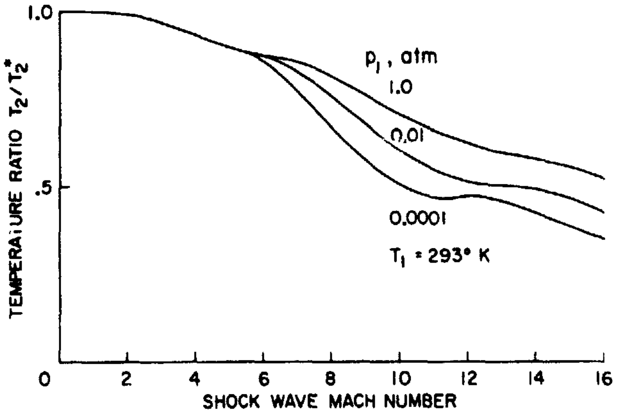
This is approximately the usual test time available in the shock tube; at longer times a compression or expansion wave produced by the shock-interface interaction feeds into the test gas. In principle, some additional test time is available before the reflected wave reaches the end wall, but in practice some mixing always occurs at the interface and the reflected perturbation feeds into the test gas somewhat sooner than the above. The result of these two counteracting effects is that equation (10.69) is found to give a reasonable estimate for the test time except for the following cases: (a) a "tailored interface" mode of operation, to be described later, can be achieved in which the reflections from the interface are minimized and the test interval is determined by the arrival of the expansion wave E_a or E_c (fig. 10.3(a)); and (b) at very high shock speeds the mixing region can become so broad that it consumes much of the test region.



(a) Pressure ratio.



(b) Density ratio.



(c) Temperature ratio.

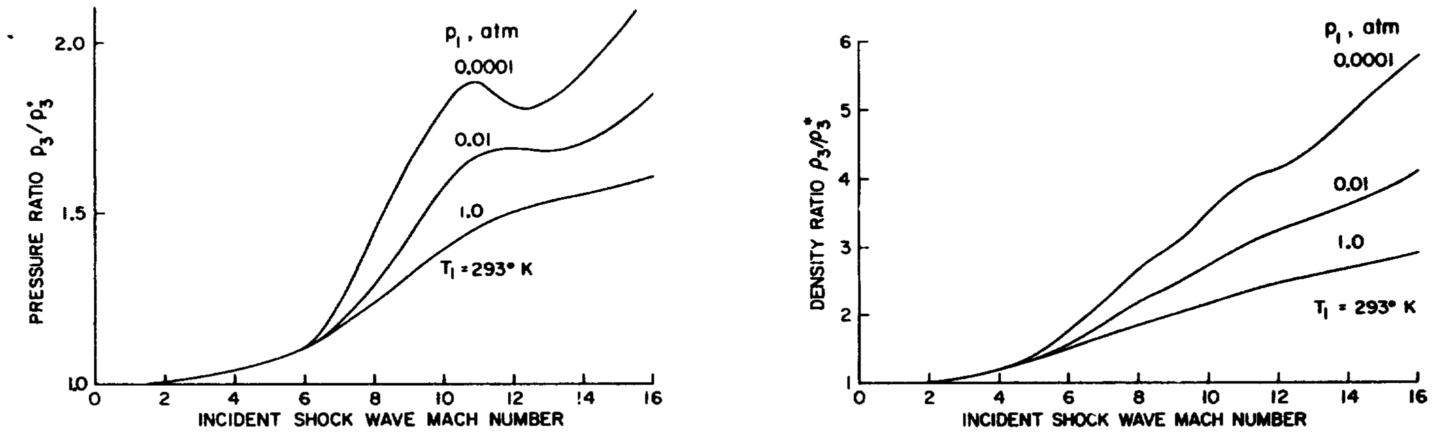
Figure 10.8.- Ratios, normal shock properties in air to ideal gas values.

Results of some calculations for the incident shock moving into air at an initial temperature $T_1 = 293°$ K are given in figure 10.8. The quantities plotted are normalized by the ideal gas value for $\gamma = 1.4$. In this way, the values remain close to unity and one can interpolate between the constant pressure curves with reasonable accuracy. The interpolation is almost linear with the logarithm of pressure. Note that the pressure across the normal shock is affected very little by the real gas effects, and the increase in density caused by dissociation and ionization is approximately balanced by the decrease in temperature. The decrease in temperature may be considered a result of the large thermal sink provided by the dissociation and ionization reactions. Plotted as a function of shock-wave Mach number, the results are approximately correct for other initial temperatures near 300° K. Properties of the air following the reflected shock are given in figure 10.9. The reflected shock speed given in figure 10.9(d) is somewhat lower than observed in actual practice. The boundary-layer effects tend to increase the observed reflected shock speed, both because the flow is squeezed into a somewhat smaller channel and because the shock wave bifurcates in the hot boundary-layer region so that sensors in the shock-tube wall are activated before the true shock arrives in the main channel. If the boundary-layer thickness is an appreciable fraction of the tube diameter, corrections must be applied to these calculated reflected shock properties.

Before considering the interaction of the reflected shock and the driving gas interface, consider the relations between the reservoir conditions, region 4, and the shock properties. These relations determine the properties in region 6 and thus he magnitude of the shock interaction with the interface. Only an ideal driver gas is treated because, in many cases of practical interest, the driving gas is predominantly helium, which is largely inert until ionization temperatures are reached. Even where the driving gas is nonideal, the general behavior of the nonideal gas can be approximated by use of an effective ratio of specific heats.

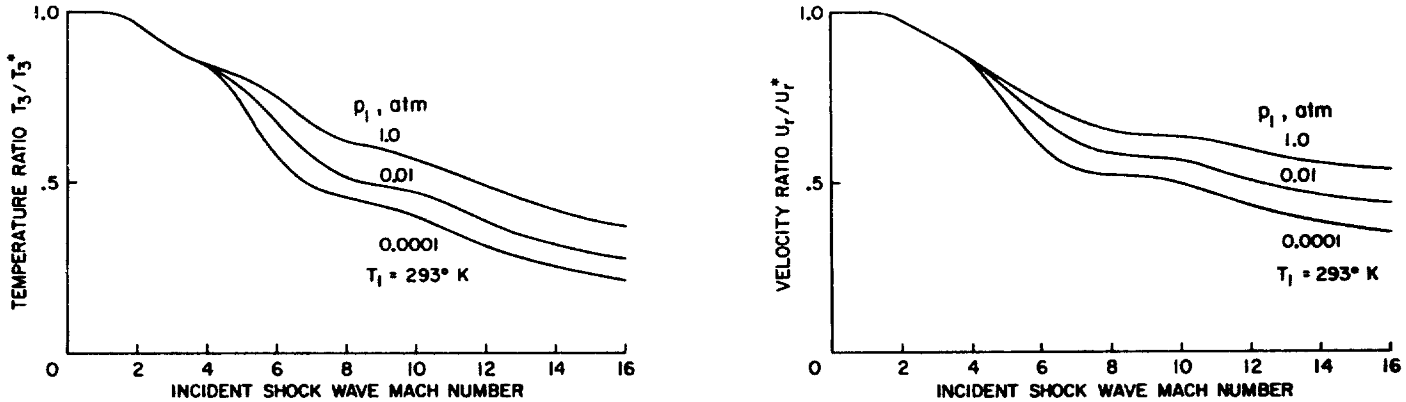
In general, the reservoir may have a cross-sectional area different from that of the shock tube. Area ratios of unity or infinity are merely special cases of the general relations that follow. When the reservoir gas is suddenly released into the lower pressure shock-tube gas, an expansion wave E_a propagates down the tube following the shock S and the interface I (fig. 10.3). This expansion is a nonsteady but isentropic process that accelerates the reservoir gas to its velocity at the interface; the expansion wave actually moves upstream against the flow. At the area transition between reservoir and shock tube, another isentropic expansion E_s is established which rapidly becomes steady state. If the transition section is short, for practical purposes, we may consider this expansion to reach its steady state instantaneously. The downstream side of this expansion terminates at the sonic line where the local Mach number is unity. Finally, another unsteady, isentropic expansion E_b propagates into the reservoir and accelerates the gas toward the entrance to the shock tube. Before proceding with the analysis, it may be helpful to recall the difference between steady-state and nonsteady expansions. Across the steady-state expansion, the energy per unit mass of gas is conserved:

$$\frac{u^2}{2} = h_o - h = C_p(T_o - T) \qquad (10.70)$$



(a) Pressure ratio.

(b) Density ratio.



(c) Temperature ratio.

(d) Reflected shock velocity ratio.

Figure 10.9.- Ratios, reflected shock properties in air to ideal gas values.

where h_o is the conserved stagnation enthalpy. The Mach number of the flow is given by

$$M^2 = \frac{u^2}{\gamma RT} = \frac{2C_p}{\gamma R}\left(\frac{T_o}{T} - 1\right) = \frac{2}{\gamma - 1}\left(\frac{T_o}{T} - 1\right) \qquad (10.71)$$

Since the flow is isentropic,

$$\frac{T_o}{T} = \left(\frac{p_o}{p}\right)^{(\gamma-1)/\gamma} \qquad (10.72)$$

where

$$\frac{p}{p_o} = \left(1 + \frac{\gamma - 1}{2} M^2\right)^{-\gamma/(\gamma-1)} \qquad (10.73)$$

Equation (10.73) is the steady-state expansion relation between p and M, where p_o is the pressure on the high-pressure side of the expansion, that is, the stagnation pressure in a frame of reference at rest with respect to the gas. An alternative form of equation (10.73) is

$$\frac{p}{p_o} = \left(1 - \frac{\gamma - 1}{2} M_o{}^2\right)^{\gamma/(\gamma-1)} \qquad (10.73a)$$

where $M_o = u/a_o = u/(\gamma RT_o)^{1/2}$, that is, a Mach number referred to the stagnation speed of sound rather than the local sound speed.

For nonsteady expansions, equation (10.70) does not apply to a fixed position relative to the gas. To obtain the velocity produced by a nonsteady expansion, the characteristic equation is integrated along a constant isentrope (see ref. 1):

$$u - u_o = -\int_{p_o}^{p} \frac{dp}{\rho a} \qquad (10.74)$$

The acoustic impedance for ideal gases is

$$\rho a = \rho_o a_o \left(\frac{p}{p_o}\right)^{(\gamma+1)/2\gamma} \qquad (10.75)$$

Thus

$$u - u_o = -\frac{p_o}{\rho_o a_o}\int_1^{p/p_o} y^{-(\gamma+1)/2\gamma}\, dy \qquad (10.76)$$

Integrate and substitute $a_o = (\gamma p_o/\rho_o)^{1/2}$ to obtain

$$u - u_o = \frac{2a_o}{\gamma - 1}\left[1 - \left(\frac{p}{p_o}\right)^{(\gamma-1)/2\gamma}\right] \qquad (10.77)$$

In terms of a Mach number M defined by the change in velocity $u - u_o$,

$$M = \frac{u - u_o}{a} = \frac{2}{\gamma - 1}\left(\frac{a_o}{a}\right)\left[1 - \left(\frac{p}{p_o}\right)^{(\gamma-1)/2\gamma}\right] \qquad (10.78)$$

and since for ideal gas

$$\frac{a_o}{a} = \left(\frac{T_o}{T}\right)^{1/2} = \left(\frac{p_o}{p}\right)^{(\gamma-1)/2\gamma} \qquad (10.79)$$

the unsteady expansion relation between p and M is

$$\frac{p}{p_o} = \left(1 + \frac{\gamma - 1}{2} M\right)^{-2\gamma/(\gamma-1)} \qquad (10.80)$$

An alternative form of equation (10.80) is

$$\frac{p}{p_o} = \left(1 - \frac{\gamma - 1}{2} M_o\right)^{2\gamma/(\gamma-1)} \qquad (10.80a)$$

where $M_o = (u - u_o)/a_o$.

With the difference between equations (10.73) and (10.80) clearly in mind, proceed to calculate the Mach number M_5 from

$$\frac{A_4}{A_1} = \frac{A_4}{A^*} = \frac{1}{M_5}\left[\frac{2 + (\gamma - 1)M_5^2}{\gamma + 1}\right]^{(\gamma+1)/[2(\gamma-1)]} \qquad (10.81)$$

Since the solution for M_5 requires iteration, a more straightforward procedure specifies M_5 and calculates the area ratio A_{41} that corresponds to this Mach number. The pressure ratio for the rarefaction wave that accelerates the gas from rest in state 4 to the velocity M_5 is given by the nonsteady expansion

$$\frac{p_4}{p_5} = \left(1 + \frac{\gamma - 1}{2} M_5\right)^{2\gamma/(\gamma-1)} \qquad (10.82)$$

Further acceleration to the sonic velocity requires a pressure ratio given by the steady relation

$$\frac{p_5^0}{p^*} = \left(\frac{\gamma + 1}{2}\right)^{\gamma/(\gamma-1)} \qquad (10.83)$$

where p^* is the pressure at the sonic line and p_5^0 is a conserved stagnation pressure for region 5 defined by

$$\frac{p_5{}^0}{p_5} = \left(1 + \frac{\gamma - 1}{2} M_5{}^2\right)^{\gamma/(\gamma-1)} \tag{10.84}$$

Thus

$$\frac{p_5}{p^*} = \left[\frac{\gamma + 1}{2 + (\gamma - 1)M_5{}^2}\right]^{\gamma/(\gamma-1)} \tag{10.85}$$

Finally, to accelerate the gas further to M_6, a second nonsteady rarefaction (see eq. (10.80)) is required so that

$$\frac{p^*}{p_6} = \left[\frac{2 + (\gamma - 1)M_6}{\gamma + 1}\right]^{2\gamma/(\gamma-1)} \tag{10.86}$$

The total pressure drop from region 4 to 6 is obtained by multiplying equations (10.82), (10.85), and (10.86):

$$\frac{p_4}{p_6} = \frac{p_4}{p_5}\frac{p_5}{p^*}\frac{p^*}{p_6} \tag{10.87}$$

Since the entire set of expansions, both steady and unsteady, is isentropic, the temperature ratio is

$$\frac{T_4}{T_6} = \left(\frac{p_4}{p_6}\right)^{(\gamma-1)/\gamma} \tag{10.88}$$

All other properties in region 6 are determined accordingly. There cannot be a discontinuity in pressure or velocity across the interface; therefore, $p_6 = p_2$ and $u_6 = u_2$. Thus all conditions in regions 2 and 1 are determined by the choice of M_6.

When $M_5 = 0$, the area ratio A_{41} becomes infinite and the expansion wave E_b disappears. Actually, the pressure drop $(P_{45} - 1)$ becomes very small for area ratios of the order 10, and a chamber with area ratio A_{41} greater than 10 functions essentially as an infinite chamber if it also has sufficient volume that the weak but finite expansion waves, produced in the chamber by the exhaust of reservoir gas, do not decrease the pressure appreciably. The required reservoir volume is thus a function of shock-tube length. The strength of the expansion E_c produced by reflection of E_b from the end of the reservoir is calculated as follows: After the expansion reflects from the wall, it decelerates the gas to zero velocity again in region 9, that is, the change in velocity is $-V_5$. The speed of sound on the high-pressure side of the wave is a_5. Then equation (10.80a) becomes, with notation appropriately changed,

$$\frac{p_9}{p_5} = \left(1 - \frac{\gamma - 1}{2} M_5\right)^{2\gamma/(\gamma-1)} \tag{10.89}$$

When $M_5 = 1$, the area ratio A_{41} is unity and the steady-state expansion E_8 disappears; the remaining expansions become a single nonsteady expansion for which the pressure drop is given by an equation of the form (10.80).

Problem 10.2: For a shock tube with area ratio $A_{41} = 1$ and ideal gas behavior, show that the relation between shock strength p_{21} and reservoir pressure ratio p_{41} is given by

$$p_{41} = \left[\frac{p_{21}}{1 - (p_{21} - 1)\sqrt{\dfrac{(\alpha_1 - 1)T_{14}}{(\alpha_4{}^2 - 1)(\alpha_1 p_{21} + 1)}}}\right]^{\alpha_4+1}$$

Generally, when the shock wave that reflects from the end of the shock tube interacts with the interface I, it is partly transmitted and partly reflected. The reflected part may be either an expansion or a compression wave, depending on the relative energy levels of the two gases. To obtain long testing times, one is particularly interested in the special case where the reflected part vanishes. In figure 10.3, the boundary conditions that correspond to no reflection at the interface require that $p_3 = p_7$ and $v_3 = v_7 = 0$. When v_7 vanishes, the shock velocity is W_7 and the velocity with which the air from region 6 enters the shock is

$$W_6 = W_7 + v_6 = W_7 + (u_1 - u_2) \tag{10.90}$$

Thus (see eq. (10.45)),

$$(W_6 - W_7)^2 = (u_1 - u_2)^2 = \frac{p_1}{\rho_1}(p_{21} - 1)(1 - \rho_{12}) = \frac{p_6}{\rho_6}(p_{76} - 1)(1 - \rho_{67}) \tag{10.91}$$

From the equality of pressures $p_7 = p_3$ and $p_6 = p_2$, there results

$$(p_{21} - 1)(1 - \rho_{12}) = p_{21}\rho_{16}(p_{32} - 1)(1 - \rho_{67}) \tag{10.92}$$

The basic shock-wave equation, equation (10.39), across the shock separating regions 6 and 7, becomes

$$(p_{32} - 1)(\rho_{67} + 1) = (\alpha_6 + 1)(h_{76} - 1) \tag{10.93}$$

Equations (10.92) and (10.93) are two relations between three unknowns ρ_{16}, ρ_{67}, and h_{76}. The third relation required is again given by the equation of state:

$$\rho = \rho(p,h) \tag{10.94}$$

Generally, equations (10.92), (10.93), and (10.94) must be solved by an iteration procedure as for the incident and reflected shock properties in a real gas. In some cases of practical interest, the gas in region 6 is at a relatively low temperature where the ideal gas relation holds. This is particularly true where the driver gas is largely an inert gas such as helium. Then equation (10.94) can be expressed (see eq. (10.41)) as

$$\frac{p}{\rho} = \frac{2}{\alpha + 1} h \tag{10.94a}$$

where α is a constant. Then

$$\rho_{67} = \frac{h_{76}}{p_{76}} \tag{10.94b}$$

and the shock-wave equation (10.93) becomes

$$(p_{76} - 1)\left(\frac{h_{76}}{p_{76}} + 1\right) = (\alpha_6 + 1)(h_{76} - 1) \tag{10.93a}$$

Thus the enthalpy and density ratios are

$$h_{76} = \frac{p_{32} + \alpha_6}{\alpha_6 + p_{23}} \tag{10.95}$$

$$\rho_{67} = \frac{p_{32} + \alpha_6}{1 + \alpha_6 p_{32}} \tag{10.96}$$

If the gas in region 1 is also at a temperature low enough to behave ideally, one can substitute $(p_1/\rho_1) = 2h_1/(\alpha_1 + 1)$; then

$$\frac{2h_1}{\alpha_1 + 1}(p_{21} - 1)(1 - \rho_{12}) = \frac{2h_6}{\alpha_6 + 1}(p_{32} - 1)(1 - \rho_{67}) \tag{10.97}$$

from which the enthalpy ratio is

$$h_{61} = \frac{\alpha_6 + 1}{\alpha_1 + 1}\,\frac{(p_{21} - 1)(1 - \rho_{12})}{(p_{32} - 1)(1 - \rho_{67})} \tag{10.98}$$

This is the enthalpy ratio required so that no reflection occurs at interface I. If h_{61} is larger than given in equations (10.96) and (10.98), a shock wave is reflected back toward the end of the shock tube; if it is smaller, an expansion wave is reflected. The strength of the transmitted wave adjusts itself so that a continuity of pressure and velocity is maintained across the interface.

Establishing the above conditions leads to what is called the "tailored interface" mode of shock tube operation. The advantage of this mode is that it leads to long test intervals, which can be an order of magnitude longer than the estimate given by equation (10.69). The disadvantage is that the experimenter has less flexibility in the choice of test conditions than is often desired, since only one uniquely tailored test condition can be obtained for a given initial test gas and driver gas combination, whereas an entire range of test gas pressures and temperatures can be easily obtained just by changing the driver gas pressure or enthalpy, if reflected waves from the interface are permitted. In practice, there are always some small disturbances which feed into the test gas even at tailored interface conditions, due to the fact that the interface is a mixed region rather than a true discontinuity as assumed in the analysis. However, these disturbances can often be made quite small so that a relatively steady test sample is obtained until the expansion wave E_a or E_c (fig. 10.3(a)) feeds into the test gas. Whichever expansion arrives first depends on the shock tube and reservoir lengths, of course. The test interval can be further increased by designing the ratio of the reservoir area to the shock tube area so that the returning compression wave just cancels the expansion wave E_a and is essentially attenuated to vanishing strength as it reaches the entrance to the reservoir. A perforated throttle plate can be used at the entrance to achieve this condition, while at the same time the reservoir functions essentially as an infinite gas supply where the expansion E_c vanishes. This is known as the "one-cycle shock compression" mode of operating the shock tube. Perhaps the largest, long-test-interval shock tube of this type was the 1-Foot Hypervelocity Shock Tunnel at the Ames Research Center developed by Cunningham and Kraus (ref. 10), which had a usable test interval up to 180 millisec. A spark ignited combustible mixture of H_2, O_2 and He was used to produce driver gas at 2080° K and 340 atm; the facility was extensively calibrated for tailored operation in air (ref. 11) at an initial pressure of 0.34 atm, leading to a test sample of air at 5650° K and 275 atm. This air sample was used as the reservoir driving a 1-foot diameter supersonic nozzle at a Mach number 14; the long test times were needed in this case so that models could be tested in the expanded stream for heating rates, drag coefficients, etc.

The long test intervals obtained with the tailored interface shock tube are not really needed for other types of experiments such as measurements of reaction rate processes, radiation properties of high temperature gases, etc. Modern instrumentation has such good high frequency response that such measurements can often be made in a time the order of 10 μsec or less. Thus most shock tubes are operated over a wide range of test conditions which can be obtained when tailoring is ignored. Most tubes are made less than 100 diameters in length in order to limit boundary layer effects which severely attenuate the shock speed at distances far along the tube and force the experimenter to cope with a non-constant shock velocity there.

Other practical limitations appear as one attempts to produce the very highest speed shock waves and highest temperature test gas samples. At present, the strongest shocks with adequate test intervals are produced by heating hydrogen driver gas with a high-voltage, high-current electric discharge. Discharges of 40 kV with peak currents of 5×10^5 amperes have been used, producing shock velocities up to about 50 km/sec in hydrogen test gas initially at room temperature and one torr pressure (refs. 12 and 13), with usable test intervals the order of 5 μsec. Still higher velocities are possible, but only at much reduced pressure and with vanishingly small test intervals. For example, another technique of producing strong shocks with velocities greater than 60 km/sec makes use of shaped charge explosives (refs. 14 and 15), but again produces very short test intervals. However. this situation is changing rapidly with methods of tailoring the arc discharge to the time changes in driver gas properties and by mass addition to the driver gas during the discharge process (ref. 13). Thus still higher shock speeds in test gases with usable pressure and reasonable test intervals are anticipated in the future. The conditions necessary to test the full range of space probe entry into heavy planet atomspheres (Jupiter, Saturn, Uranus) appear to be achievable.

10.10 CONCLUDING REMARKS

Equilibrium thermodynamic properties of real gases in shock-tube flow can be calculated with good accuracy, and these solutions are often used with measured shock velocities to establish the properties of high-temperature gases produced in shock tubes for various test purposes. Generally, the shock wave reflected from the end wall of a tube travels at faster speed than calculated for one-dimensional flow because the boundary layer built up by the incoming flow effectively reduces the channel area, but if the gas properties are related to the measured shock velocities they can be assessed quite accurately.

Shock tubes are, of course, widely used to measure nonequilibrium rate processes in which the experimenter measures a rate of approach toward equilibrium and deduces a time constant or rate coefficient for the process or processes taking place in the shock-excited gas. To pursue these problems further, we must leave the comfortable realm of equilibrium where the relations between variables are independent of the processes involved and tackle the far more difficult problem of modeling rate processes that occur under nonequilibrium conditions. These produce, for example, the transfer of mass, momentum, energy, or charge through gases when nonequilibrium gradients in species density, velocity, and temperature occur. If the changes in flow properties are rapid compared with chemical relaxation times, then finite rate chemistry must be included for the relaxation of rotational energy, vibrational energy, electronic energy, and chemical species concentration. Finally, the rate of radiant energy transfer through gases depends on the radiation absorbtion and emission rates of the excited atomic and molecular species present. This takes us beyond the bounds of this book, but the material included here is a prerequisite to an analysis of these fascinating subjects.

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