

Chapter 12 Statistical Mechanics for Independent-Particle Systems

Framework of the Chapter

12.1 Introduction

I. Principles of Statistical Mechanics

12.2 Description of Microscopic States

12.3 Fundamental Postulates of Statistical Mechanics

12.4 The Most Probable Distribution

II. Statistical Distributions of Independent-Particle Systems

12.5 Maxwell-Boltzmann Distribution

12.6 Molecular Partition Function

III. Thermodynamic Properties of Independent-Particle Systems

12.7 Thermodynamic Functions of Independent-Particle Systems

12.8 Standard Molar Heat Capacity of Gases

12.9 Heat Capacity of Crystals

12.10 Standard Molar Entropy of Gases

12.11 Standard Equilibrium Constant of Gaseous Reactions

Brief History, Concluding Remarks, General Problems, Numerical Problems

Framework of the Chapter

This chapter provides general principles of equilibrium at the transition level from microscopic to macroscopic. The principles can be applied to expound the essentials of those thermodynamic laws and to predict the macroscopic equilibrium properties with the incorporation of the microscopic characteristic properties of substances. At first, we introduce the principles of statistical mechanics including the fundamental postulates and the fundamental methods. Then we derive the Maxwell-Boltzmann distribution which is the center of this chapter and can be regarded as the fundamental equation. Finally, the applications are discussed. The chapter is divided into three parts:

I. Principles of Statistical Mechanics We are dealing primarily with the independent-particle systems in this chapter and will further discuss the dependent-particle systems in the next chapter. We have to first distinguish the former from the latter. Also we have to know the difference between the description of microscopic states by classical mechanics and that by quantum mechanics. In this chapter we adopt quantum mechanical description including the translational, rotational, vibrational and electronic energy levels, and the corresponding quantum numbers. All these are the microscopic characteristic properties of substances that have to be incorporated with the general principles at the transition level for the independent-particle systems (12.2). The Part III "Structure" of this book is helpful for learning. However, even if you haven't learnt the Part III, it is still going as well because a brief review is provided.

(1) **Three Fundamental Postulates of Statistical Mechanics** As a whole, the three postulates form the foundation of the statistical mechanics. However, the third one, the postulate of equal a priori probabilities, is especially

important because it makes possible to obtain the macroscopic properties by the statistical average of the microscopic properties (12.3).

(2) **Fundamental Methods in Statistical Mechanics** Adopting the distributions especially the most probable distribution and adopting the maximum-term are two fundamental methods which make the connection between the microscopic states and the macroscopic state turn to be operable. The distribution is the intermediate stage between the microscopic states and the macroscopic state, the most probable distribution represents all the possible distributions in an equilibrium system. The maximum-term method allows using the thermodynamic probability of the most probable distribution to replace that of the macroscopic state (12.4).

II. Statistical Distributions of Independent-Particle Systems

(1) **Maxwell-Boltzmann Distribution** It is the most popular distribution for the equilibrium states of the independent-particle systems. The fundamental formulae are derived. For the more rigorous Bose-Einstein distribution and Fermi-Dirac distribution, a brief description is presented. The connections among these three distributions are also discussed (12.5).

(2) **Molecular Partition Functions** The molecular partition functions embody the rules of statistical distributions collectively. The functions can be decomposed into contributions of the translational, rotational, vibrational and electronic motions and expressed as the corresponding molecular characteristic properties on the one hand, on the other hand, they relate closely with the macroscopic properties. Calculations of the translational, rotational and vibrational partition functions for diatomic molecules are presented (12.6).

III. Thermodynamic Properties of Independent-Particle Systems

This part concerns the application of the theory. The general principles incorporated with the microscopic molecular characteristic properties are applied to interpret the meanings of the energy, the entropy and other thermodynamic functions, and to predict those macroscopic properties.

(1) **Equations Connecting Thermodynamic Properties with Molecular Partition Functions** The equations connecting the energy, the entropy, as well as other thermodynamic functions and the molecular partition functions are derived. The equipartition theorem of energy in terms of the degree of freedom, and the Boltzmann relation are also briefly introduced (12.7).

(2) **Applications** Various calculation methods with examples for the standard molar heat capacity of gases (12.8), the heat capacity of crystals by the Einstein model and the Debye model (12.9), the standard molar entropy (12.10) and the standard equilibrium constant of gaseous reactions are presented (12.11).

12.1 Introduction

1. The Role of Statistical Mechanics in Physical Chemistry

Limitations of the General Principles at Macroscopic Level The object of studies of the chemical thermodynamics, the transport phenomena and the chemical kinetics is the macroscopic systems composed of a large number of microscopic particles. The general principles obtained by which

various macroscopic properties are related are highly reliable. However, because they do not involve the microscopic structures of matters and the microscopic movements, therefore, they can not reveal the nature of the matters. To study the equilibrium properties such as pVT relations and heat capacity, the transport properties such as thermal conductivity, viscosity and diffusion coefficient, the rate properties such as reaction order, pre-exponential factor and activation energy and to provide the possibilities to predict these properties based on the microscopic nature of matters, therefore, it is necessary to enter a deeper level, i.e., the transition level from microscopic to macroscopic.

Statistical Mechanics Provides General Principles at the Transition Level from Microscopic to Macroscopic Statistical mechanics is a branch of physics with the following fundamental starting points:

(1) The movement of a single microscopic particle (molecule, ion, electron, photon, etc) is a **mechanical phenomenon** with reversibility and irrelevant to the concept of temperature. The particles in the system transport energy among one another by collisions or radiations.

(2) Macroscopic substances are composed of a large number of microscopic particles and exhibit temperature. Heat transfer occurs between substances with different temperatures. The macroscopic movements such as pVT changes, transport processes and chemical reactions are all temperature dependent and with irreversibility. They belong to the **thermal phenomena**.

(3) The object for studies of the statistical mechanics is also the macroscopic systems composed of a large number of microscopic particles. However, starting from the microscopic movements of matters, the studies obtain various macroscopic properties from the corresponding microscopic properties of particle movements by using the method of statistical average. Therefore, the studies can not only reveal the nature of the macroscopic thermal phenomena, but also provide extensive possibilities to predict various macroscopic properties from the microscopic properties. The statistical mechanics is just like a bridge linking up the macroscopic and the microscopic properties of matters, linking up the thermodynamics, transport

phenomena, chemical kinetics and the quantum mechanics, which makes the physical chemistry an integrated branch of chemical science.

(4) When applying the general principles of statistical mechanics to study the macroscopic equilibrium and rate properties, similar to other general principles, the characteristic properties of matters should be imported or incorporated. Here, we should import or incorporate the microscopic characteristic properties of matters, for examples, the translational energy levels determined by the mass of molecules, the rotational energy levels by the moment of inertia, the vibrational energy levels by the characteristic frequency, the electronic energy levels, the intermolecular forces, and the collision cross-section, the potential-energy surface of the reaction systems. Because of the complexities of the microscopic movements, models are usually adopted such as the translational particle, the rigid rotator, the simple harmonic oscillator, etc.

General Principles at Microscopic Level To study the microscopic characteristic properties of matters theoretically is the task of the next lower level, the microscopic level based on the quantum mechanics. The Part III, “The Structure” in this book has already provided a rudimentary introduction.

2. Several Terminologies

Statistical Physics It is the statistical mechanics in other words. It has two categories, the equilibrium one and the non-equilibrium one.

Statistical Thermodynamics It is the equilibrium statistical mechanics in other words.

Independent-Particle System It is a system composed of particles without any interactions among them except the elastic collisions. In reality, a system without interactions completely among particles does not exist. But when the interactions are very weak that are negligible, the system can be called approximately an independent-particle system, or called a **nearly independent-particle system**.

Dependent-Particle System It is a system with interactions among the composed particles.

Non-Localized-Particle System It is a system in which the

composed particles can move in the whole space of the system. The ideal gas is an independent non-localized-particle system, while the real gas or liquid is a dependent non-localized-particle system.

Localized-Particle System It is a system in which the composed particles can move only in a small region around fixed positions such as atoms, molecules or ions in a crystal, gas molecules adsorbed and fixed on a solid surface.

I. Principles of Statistical Mechanics

12.2 Description of Microscopic States

1. Macroscopic State and Microscopic State

When we say that a system composed of a large number of molecules or particles is in a certain state, usually, indicating a macroscopic equilibrium state. In this state, various macroscopic properties such as T , p , U , S all have certain fixed values. However, investigating microscopically, the system is still fast changing in this macroscopic state, every one of the molecules is changing its moving status uninterruptedly, and the microscopic state of the whole system is then changing continuously. A microscopic state is the sum of the instantaneous moving status of every one of the molecules or particles in a system at a certain time. It determines the microscopic properties or the microscopic physical quantities of the system.

2. Classification of Molecular Movements

(1) **External Movements** The **translational motions** of molecules with the molecule regarded as a whole are classified as external movements. The corresponding energies are the translational energy ε_t of molecules and the interaction potential energy ε_p among different molecules.

(2) **Internal Movements** The relative motions among various particles composing a molecule are classified as internal movements. They can be distinguished by the **rotation** and the **vibration** of a molecule, electrons moving around the nucleus and electron spins in an atom, the nuclear spin and the movements of particles inside the nucleus. Correspondingly, there are the rotational energy ε_r , the vibrational energy ε_v ,

the electronic energy \mathcal{E}_e , and the nuclear energy \mathcal{E}_n .

Thermal Movements The motion of a single molecule is a mechanical movement. For a great number of molecules, the energies of motions are allocated on or sheared by various molecules with a temperature dependent distribution. Therefore, the motions are called the thermal movements. Taking the translational motion for example, the number of molecules with higher translational energy increases as raising the temperature, while the number of molecules with lower translational energy decreases. Therefore, the translational motion is a thermal movement. The rotational and the vibrational motions are thermal movements, too. The electronic and the nuclear motions are also thermal movements in principle. However, because of the large energy spacing between the different electronic or nuclear energy levels, the transition or excitation of energy levels is difficult to happen in ordinary temperature change. Therefore, these motions are generally called the **non-thermal movements**.

Degree of Freedom of Movement The degree of freedom of movement has been explained in 11.3.4 of Chap.11, it is different from the degree of freedom in the phase rule elucidated in Chap.3. For a molecule composed of n atoms, usually it has three translational degrees of freedom in three directions of x , y and z axes, three rotational degrees of freedom corresponding to the rotations around the three axes, and $3n-6$ vibrational degrees of freedom, totally $3n$ degrees of freedom of movement. For linear molecules, besides the three translational degrees, the rotational degrees reduce to two because the energy of the rotation around the linear axis is negligible, correspondingly, the degrees of freedom of vibration turns to $3n-5$, totally a molecule still has $3n$ degrees of freedom of movement.

3. Classical Mechanical Description of Microscopic States

Generalized Coordinates and Generalized Momentums For every one degree of freedom, we need two variables to fix its moving state. For examples, the two variables are the coordinate x and the partial momentum p_x for the translation in x direction, the azimuth θ and the angular momentum p_r for the rotation around an axis, the relative distance d and the relative momentum p_v (the product of the reduced mass and the variation

rate of the relative distance with time) for the vibration of two particles. In summary, for any one degree of freedom i , we can use a generalized coordinate q_i and a generalized momentum p_i to describe its moving state.

Molecular Phase Space (μ space) Suppose a molecule has r degrees of freedom, the moving state of the molecule is described by r generalized coordinates and r generalized momentums. The molecular phase space is then defined as a $2r$ -dimensional space with r generalized coordinates and r generalized momentums as its axes. A molecule at a moving state is represented by a point in this space and the N molecules in a system are represented by N points. (Strictly speaking, a point is meaningless, it should be a small region

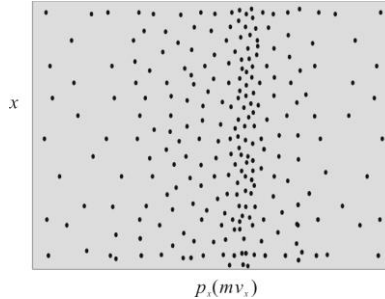


Figure 12-1 Two-dimensional molecular phase space (\cdot represents a molecule or a particle)

determined by the uncertainty principle, referring to 9.3.3). The sum of the N points represents a microscopic state of the system and the movements of the N points represent the change of the microscopic state. Figure 12-1 depicts a molecular phase space with x and $p_x(mv_x)$ as axes for a one-dimensional translational-particle system. The Figure shows the coordinate x and the corresponding momentum p_x for all the molecules at an instantaneous moment and the whole picture represents a microscopic state. The Figure also shows that the molecules are distributed more or less homogeneously along the x axis but notably concentrated in a certain momentum region along the p_x axis with only a few molecules having extremely large or excessively small momentums.

Phase Space (Γ space) For N molecules as a whole, they have altogether rN generalized coordinates and rN generalized momentums. The phase space is then defined as a $2rN$ -dimensional space with rN generalized coordinates and rN generalized momentums as its axes. Any point in this space represents a microscopic state of the system that the generalized coordinate and the generalized momentum as well as the moving status of everyone of the molecules are fixed. The moving trajectory of the point

represents the change of the microscopic state of the system.

4. Quantum Mechanical Description of Microscopic States

Microscopic States of Independent-Particle Systems

The movements of microscopic particles are quantized, the microscopic state of a system is a quantum state described by the wave function of the system. For an independent-particle system, the wave function of the system can be replaced by the product of the N molecular wave functions, and the quantum state of the system can be represented by the quantum states of N independent molecules themselves. The quantum state of each molecule can be further resolved approximately into the translational, the rotational and the vibrational as well as the electronic and the nuclear quantum states. These quantum states have a certain energies called energy levels usually with discrete character. When two or more quantum states have the same energy, the energy level is called the **degenerate energy level** and the number of the quantum states is called the **degeneracy**. When any one of the molecules transits from a quantum state to another, the moving status of the molecule changes and the microscopic state of the system changes correspondingly. In the following we will review briefly various energy levels. The subscripts t, r, v, e and n represent translation, rotation, vibration, electron and nucleus, respectively. For details refer to Chapter 9.

(1) **Translational Energy Levels** Particles in translational motions without interactions among one another are called the **translational particles**. Suppose a translational particle moving freely in a three-dimensional rectangular box with sizes of l_x , l_y and l_z along the three axes, according to Eq.(9-47), the translational energy derived is

$$\varepsilon_t = \frac{h^2}{8m} \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right) \quad (12-1)$$

where m is the mass, n_x , n_y , n_z are the **translational quantum numbers** relevant to the directions of x , y , z axes which can only take positive integers 1, 2, 3 ... greater than zero, different values of n_x , n_y , n_z represent different translational quantum states. $h = 0.66260755 \times 10^{-33} \text{J}\cdot\text{s}$ is the Planck constant. For a cubic box, $l_x = l_y = l_z = V^{1/3}$,

$$\varepsilon_t = \frac{h^2}{8mV^{2/3}}(n_x^2 + n_y^2 + n_z^2) \quad (12-2)$$

Eqs.(12-1, 12-2) indicate that the translational energy levels are not continuous, they can only change discretely by varying the translational quantum number, and the spacing between different energy levels is determined by the mass of the translational particle and the volume of the system. The larger the mass and the volume, the smaller the spacing will be. Eq.(12-2) also indicates that some energy levels are degenerate. For example, the three quantum states 211, 121 and 112 have the same energy and the degeneracy of the energy level is 3.

(2) **Rotational Energy Levels** According to Eq.(9-55), the rotational energy ε_r derived for a linear rigid rotator is

$$\varepsilon_r = \frac{h^2}{8\pi^2 I} J(J+1) \quad (12-3)$$

where J is the **rotational quantum number** which can take only 0 and positive integers 1, 2, 3 ..., I is the moment of inertia. Eq.(12-3) indicates that the rotational energy levels are also discrete, the larger the moment of inertia, the smaller the spacing between the neighboring levels. Because the orientation of the rotational angular momentum in space is also quantized, for each J value, the orientation can have $2J+1$ different directions in space, therefore, besides $J=0$, the rotational energy levels are degenerate, the degeneracy is $2J+1$.

(3) **Vibrational Energy Levels** According to Eq.(9-64), the vibrational energy ε_v derived for a simple harmonic oscillator is

$$\varepsilon_v = (v + \frac{1}{2})h\nu \quad (12-4)$$

where ν is the **vibrational quantum number** which can take only 0 and positive integers 1, 2, 3 ..., ν (the same as ν_0 in Chapter 9) is the **vibration frequency**. Eq.(12-4) indicates that the vibrational energy levels are also discrete with equal spacing between the neighboring levels, the smaller the vibration frequency, the smaller spacing will be. When $\nu=0$, ε_0 does not equal 0 but a value of $h\nu/2$ called the **zero point energy**. The vibrational energy levels are non-degenerate.

(4) **Energy-Level Spacing** Figure 12-2 depicts the relative

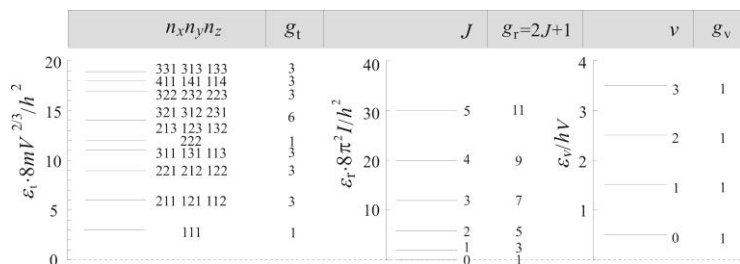


Figure 12-2 Translational, rotational and vibrational energy levels

positions for the translational, the rotational and the vibrational energy levels with their quantum numbers noted. The orders of magnitude have large differences for these three energy levels. Taking for example a N_2 molecule moving in a container with a volume of $V=10^{-6}m^3$ at ambient temperature, the spacing for the three energy levels is about:

$$\Delta\epsilon_t \approx 10^{-19} kT, \quad \Delta\epsilon_r \approx 10^{-2} kT, \quad \Delta\epsilon_v \approx 10kT$$

where k is the Boltzmann constant, $k=R/L=13.80658 \times 10^{-24} J \cdot K^{-1}$, kT is about $4 \times 10^{-21} J$. The spacing of the translational energy levels is the smallest that the levels can usually be treated in terms of classical mechanics approximately as a continuous variable.

(5) Molecular Energy Levels The energy or energy level of a molecule can be treated approximately in terms of a simple summation of the energies or energy levels of various forms of motion,

$$\epsilon = \epsilon_t + \epsilon_r + \epsilon_v + \epsilon_e + \epsilon_n \quad (12-5)$$

Correspondingly, the degeneracy g of a molecular energy level is a product of the degeneracy of energy levels of various forms of motion, ($g_v=1$)

$$g = g_t \cdot g_r \cdot g_v \cdot g_e \cdot g_n = g_t \cdot g_r \cdot g_e \cdot g_n \quad (12-6)$$

Dependent-Particle Systems Because of the intermolecular interactions, usually we adopt the classical mechanics and the quantum mechanics to describe the external and internal movements, respectively.

12.3 Fundamental Postulates of Statistical Mechanics

Similar to the thermodynamics and the quantum mechanics, the theoretical framework of the statistical mechanics is also constructed on the basis of several fundamental postulates. Thermodynamics has four laws, quantum mechanics has four fundamental postulates, for the statistical

mechanics, it has three fundamental postulates. Fundamental postulates can not be proved by other theories. They were induced and abstracted from the practice of the corresponding studies, and their corollaries have been or can be verified from the practice.

1. The First Postulate: A macroscopic state corresponds to a certain generally a large number of microscopic states, each of them appears in terms of a certain probability.

The object of studies of the statistical mechanics is the system composed of a large number of molecules. If only several molecules are concerned, the principles are discussed by the classical mechanics or the quantum mechanics. As has been mentioned above, any tiny change of the coordinate or momentum of any one molecule, or any change of the quantum state, means a change of the microscopic state. We can then imagine that the number of the microscopic states should be generally very large. However, in these microscopic states with a great number, only those in accordance with the constraints inherent in the macroscopic state are possible to appear. Therefore, although the relevant number of states is great yet it is limited. What is more important is that the change of those microscopic states observes statistical principles. A microscopic state appears with a certain probability in a certain condition.

2. The Second Postulate: A macroscopic mechanical quantity is the statistical average of the corresponding microscopic quantities.

Mechanical Quantities and Non-Mechanical Quantities There are two categories of the macroscopic properties of systems. The one includes those properties that can find their corresponding microscopic properties at molecular level such as energy, density, pressure, etc. These properties are called the **mechanical quantities**. The other includes those properties that do not have clearly corresponding microscopic properties such as temperature, entropy, Gibbs function, chemical potential, etc. These properties are called the **non-mechanical quantities**. We can talk about the energy of an individual molecule, the local density in a very small region, the force exerted by a molecule when collides the wall, but we can not define the temperature or the entropy for an individual molecule.

Mathematical Expression of the Second Postulate For a mechanical quantity B , the corresponding microscopic quantity at a microscopic state i is B_i , then the second postulate can be expressed by

$$B = \langle B \rangle = \sum_i B_i P_i \quad (12-7)$$

where $\langle \rangle$ represents statistical average, P_i is the probability of appearance of the microscopic state i , $\sum_i P_i = 1$, \sum_i denotes a summation over all the possible appearances of the microscopic states. Eq.(12-7) connects a macroscopic property with its corresponding microscopic properties indicating that the statistical mechanics plays the role of a bridge. For the non-mechanical quantities, we will show later that they can be obtained by comparison with the thermodynamic results based on the calculations of mechanical quantities.

Fluctuation Because of the diversity of P_i , the microscopic quantity B_i of the mechanical quantity B does not equal $\langle B \rangle$, but fluctuates around it. This phenomenon is called the fluctuation. The extent of fluctuation can be calculated by the following equation,

$$\sigma_B^2 = \sum_i (B_i - \langle B \rangle)^2 P_i \quad (12-8)$$

where σ_B^2 is called the **variance**, σ_B corresponds to the standard deviation in statistics. Generally, the fluctuation of macroscopic quantities is too small to be detected. But in the vicinity of the critical point, the fluctuation is distinguished. For example, the critical opalescence is caused by the notable fluctuation of the density.

Statistical Average and Time Average Generally, the two averages are considered to be equivalent. However, although it is reasonable theoretically to follow the change of the microscopic state with time, it is very difficult in practice. This difficulty is avoided in Eq.(12-7) by statistical average over various possible microscopic states.

3. The Third Postulate: For every one of the microscopic states in an isolated system, they have identical probabilities of appearance. ^①

This postulate is proposed by Boltzmann L E in 1868. It is also called the **postulate of equal a priori probabilities**. Although the postulate can

^① An equivalent statement is the **Ergodic Hypothesis**: At a certain macroscopic state for an isolated system, microscopically, the system will toss and turn traveling over all the possible microscopic states. There are different views toward this hypothesis.

not be proved directly, its correctness has been verified by the consistency between many corollaries and the practices. The characteristics of an isolated system are: The number of particles N , the energy E and the volume V are kept unchanged. In the case of isolated completely from the external influences, we have no reason to say that any microscopic state will appear preferentially (a priori), this leads to the postulate intuitively. Suppose Ω is the total number of the microscopic states for a macroscopic state, the probability P_i of the appearance of any one microscopic state i is

$$P_i = 1/\Omega \quad (12-9)$$

Mutual Relations among the Three Postulates The first postulate is a prerequisite indicating that the large number of microscopic states of a system can be studied using statistical methods. The second postulate relates a macroscopic state with its corresponding microscopic states, but we need the probabilities of the appearance of these microscopic states. The third postulate is the key telling us how to estimate those probabilities.

12.4 The Most Probable Distribution

To construct a complete framework for the statistical mechanics based on the three postulates, the problem of methodology should be further solved. In the thermodynamics, we have used the method of cycle (for example, the Carnot cycle) to obtain the entropy and the irreversibility from the second law of thermodynamics. In the statistical mechanics, we adopt the method of distributions and the maximum-term method. By distributions, we can manipulate the transition from the microscopic states to a macroscopic state. By using the maximum-term, we can greatly simplify the derivation.

1. Distributions in Independent-Particle Systems, in terms of Energy Levels and in terms of Quantum States

Distributions in terms of Energy Levels A distribution of molecules on various energy levels with serial numbers $i=0, 1, 2 \dots$ is shown as:

Energy level	$\varepsilon_0, \varepsilon_1, \varepsilon_2, \dots$
--------------	--

$$\begin{array}{ll}
 \text{Degeneracy} & g_0, g_1, g_2, \dots \\
 \text{Number of molecules} & N_0, N_1, N_2, \dots
 \end{array} \quad (12-10)$$

The degeneracy g_i is the number of quantum states relevant to the energy level ε_i . The distribution indicates that the population of molecules allocated on the energy level i with an energy ε_i and a degeneracy g_i is N_i . This distribution is mostly used in this chapter.

Distributions in terms of Quantum States A distribution of molecules on various quantum states with serial numbers $h=0, 1, 2 \dots$ is shown as:

$$\begin{array}{ll}
 \text{Energy of the quantum state} & \varepsilon_0, \varepsilon_1, \varepsilon_2, \dots \\
 \text{Number of molecules} & N_0, N_1, N_2, \dots
 \end{array} \quad (12-11)$$

There is no degeneracy for the quantum state. The distribution indicates that the population of molecules allocated on the quantum state h with an energy ε_h is N_h . This distribution is equivalent to the above distribution in terms of energy levels and is also considered in this chapter on certain occasions.

Constraints Should be Satisfied for Distributions When a system is at a certain macroscopic state with a total number of molecules N , an energy E and a volume V , the system could have different distributions, but they must satisfy the following two constraints:

$$\sum_i N_i = \sum_h N_h = N \quad (12-12)$$

$$\sum_i N_i \varepsilon_i = \sum_h N_h \varepsilon_h = E \quad (12-13)$$

The first equation elucidates the conservation of particles while the second equation concerns the conservation of energy. On the constraint of a fixed volume, it is reflected on the energy of the energy levels or quantum states, as shown in Eq.(12-2), ε_i is related to V . All the distributions satisfying the above constraints are at an intermediate level between the microscopic states and a macroscopic state.

2. Relations among Macroscopic State, Distributions and Microscopic States.

A Simplified Example To establish the relations among the macroscopic state, the distributions and the microscopic states iconically, we consider a simplified system composed of three distinguishable particles. Although the statistical mechanics does not study the systems containing

only several particles, the rules obtained by the system with only three particles could be extended to systems containing a large number of particles. Suppose the energy levels of the particles have energies of 0, 1, 2 ... units with the corresponding degeneracy of 1, 2, 1 ..., respectively. If the total energy of the system is 2 units, the macroscopic state of the system is fixed completely. On this occasion, $N=3$, $E=2$ units, V is also fixed because the spacing of energy levels is determined by the nature of the particles and the volume of the system, therefore, once the energy levels are fixed, the volume of the system is also fixed. For this macroscopic state with fixed N , E , V , we can figure out how many different distributions and how many microscopic states it has.

Analogy By a Game of Throwing

Balls Because $E=2$ units, we can only consider the former three energy levels. We adopt three closely placed boxes Z , A , B to mimic the former three energy levels, referring to Figure 12-3, balls dropped into them record 0, 1, and 2 points, respectively. The box A has two compartments analogy to the degeneracy 2. Now we throw three distinguishable balls, white, gray and black, into the boxes demanding 2 points in total analogy to the above macroscopic state. Figure 12-3 depicts various possible allocations of the balls thrown in.

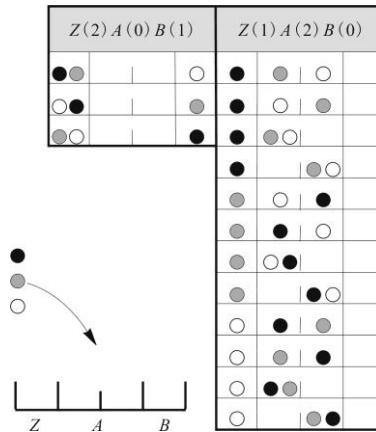


Figure 12-3 A game of throwing balls

Relations among Macroscopic State, Distributions and Microscopic States The Figure shows that there are two possible configurations or patterns for the allocation of three balls in three boxes, $Z(2)A(0)B(1)$ and $Z(1)A(2)B(0)$, corresponding to two different distributions in terms of energy levels. In each configuration, the allocation of balls still have different forms, 3 for $Z(2)A(0)B(1)$, 12 for $Z(1)A(2)B(0)$, corresponding to different microscopic states. We then can sum up: **For a macroscopic state, it is possible to have various distributions (configurations). Each**

distribution contains a certain number of microscopic states. A macroscopic state covers a fixed number of microscopic states. For the above macroscopic state, it has 2 distributions and 15 microscopic states.

Calculations for the Number of Microscopic States The number of microscopic states contained in each distribution (configuration) can be calculated by using the equations of permutation and combination. Taking the distribution $Z(1)A(2)B(0)$ for example, we assume that we first pick up any one of the three balls and put into the box Z , the number of different ways is the combination number C_3^1 , then we put the two balls remained into the box A , the number of ways is C_2^2 , further, because the box A has two compartments, for two balls allocated in two compartments, the additional number of ways is 2^2 , as for the box B , because of being empty, the number of ways is C_0^0 , the total number of different forms is then the product of the above numbers. Calculation for $Z(2)A(0)B(1)$ is similar. Finally, we have the total number of different forms or different microscopic states for the two distributions as follows:

$$\begin{aligned} Z(1)A(2)B(0): C_3^1 \cdot C_2^2 \cdot 2^2 \cdot C_0^0 &= \frac{3!}{1!2!} \cdot \frac{2!}{2!0!} \cdot 2^2 \cdot \frac{0!}{0!0!} = 12 \\ Z(2)A(0)B(1): C_3^2 \cdot C_1^0 \cdot 2^0 \cdot C_1^1 &= \frac{3!}{2!1!} \cdot \frac{0!}{1!0!} \cdot 2^0 \cdot \frac{1!}{1!0!} = 3 \end{aligned} \quad (12-14)$$

(Note: For N distinguishable bodies, selecting M of them arbitrary without taking into account the sequence, the number of different selecting ways is called the combination number, $C_N^M = N!/[M!(N-M)!]$.)

Extend to Arbitrary Distributions in terms of Energy Levels The results of the above game of throwing balls can be extended directly. For the distribution shown in Eq.(12-10) with $m+1$ energy levels, the number of microscopic states ω possessed by the distribution is

$$\begin{aligned} \omega &= C_N^{N_0} C_{N-N_0}^{N_1} C_{N-N_0-N_1}^{N_2} \cdots C_{N_m}^{N_m} g_0^{N_0} g_1^{N_1} g_2^{N_2} \cdots g_m^{N_m} \\ &= \frac{N!}{N_0! N_1! N_2! \cdots N_m!} g_0^{N_0} g_1^{N_1} g_2^{N_2} \cdots g_m^{N_m} = N! \prod_i \frac{g_i^{N_i}}{N_i!} \end{aligned} \quad (12-15)$$

Extend to a Macroscopic State with Fixed N, E, V The subscript $x(N, E, V)$ is used to represent anyone of all the possible distributions in terms of energy levels with fixed N, E and V . The corresponding number of microscopic states of the distribution is $\omega_{x(N, E, V)}$. Summing up all of them,

the total number of microscopic states Ω possessed by a macroscopic state is:

$$\Omega = \sum_{x(N,E,V)} \omega_{x(N,E,V)} = N! \sum_{x(N,E,V)} \left(\prod_i \frac{g_i^{N_i}}{N_i!} \right)_{x(N,E,V)} \quad (12-16)$$

3. Thermodynamic Probability

Definition In statistical mechanics, the number of microscopic states Ω or ω possessed by a macroscopic state or a distribution is defined as the thermodynamic probability of this macroscopic state or distribution.

Significance An independent-particle system in equilibrium with fixed N , E and V can be viewed as an isolated system. According to the hypothesis of equal a priori probabilities, the probability of the appearance is the same for every one of the microscopic states. Therefore, the number of the microscopic states possessed or the thermodynamic probability can measure the possibility of appearance of a macroscopic state or a distribution. Different from the probability which is less than 1 and is a fraction, the thermodynamic probability is always a positive integer. For a certain distribution $x(N, E, V)$, the thermodynamic probability is $\omega_{x(N,E,V)}$, in terms of Eq.(12-9), the corresponding probability $P_{x(N,E,V)}$ is

$$P_{x(N,E,V)} = \omega_{x(N,E,V)} / \Omega \quad (12-17)$$

For the above game of throwing balls, the thermodynamic probabilities ω_x of the distributions $Z(2)A(0)B(1)$ and $Z(1)A(2)B(0)$ are 3 and 12, the probabilities P_x are 3/15 and 12/15, respectively. As for the macroscopic state, three balls in Z , A , B getting 2 points, the thermodynamic probability Ω is 15, the probability P equals 1.

Example Seven independent distinguishable particles are allocated in three energy levels with energies ϵ_0 , ϵ_1 , ϵ_2 and degeneracy 1, 3, 2. The number of particles are 3, 3 and 1, respectively. How many microscopic states are possessed by this distribution?

Solution: According to Eq.(12-15),

$$\omega = N! \prod_i \left(g_i^{N_i} / N_i! \right) = 7! \times 1^3 \cdot 3^3 \cdot 2^1 / (3! \cdot 3! \cdot 1!) = 7560$$

This distribution possesses 7560 microscopic states, the thermodynamic probability is 7560.

4. The Most Probable Distribution

Definition The distribution possessing the largest number of microscopic states or with the maximum thermodynamic probability is

called the most probable distribution. In the above game of throwing balls, the most probable distribution is $Z(1)A(2)B(0)$ with $\omega_{\max}=12$, $P_{\max}=\omega_{\max}/\Omega=12/15$.

Features or Significance For a system composed of a large number of particles, the most probable distribution represents all the possible distributions. For systems with only a few particles, the most probable distribution does not have particular importance. For example, the above game of throwing three balls in Z , A and B getting 2 points, we can only say that the possibility of the appearance of $Z(1)A(2)B(0)$ is the largest, that of $Z(2)A(0)B(1)$ is still not small. However, for systems composed of a large number of particles, the situation is completely different and the most probable distribution can represent all the possible distributions. This is a strictly proved statistical rule for systems with a large number of particles.

Demonstration Suppose there are $N=1 \times 10^{24}$ distinguishable balls thrown (allocated) into a box (energy level) with two compartments of A and B (quantum states), the various distributions (in terms of quantum states) are:

$A(0)B(N), A(1)B(N-1), \dots, A(M)B(N-M), \dots, A(N-1)B(1), A(N)B(0)$

(1) Calculate Thermodynamic Probability ω for Every Distribution.

Using the above Eq.(12-15) for calculating ω of distributions, noting that the degeneracy is irrelevant to the quantum states, we obtain for $A(M)B(N-M)$,

$$\omega(M, N-M) = C_N^M = \frac{N!}{M!(N-M)!} \quad (12-18)$$

(2) Thermodynamic Probability Ω of a Macroscopic State. It is the summation of ω of various distributions,

$$\Omega = \sum_{M=0}^N \omega(M, N-M) = \sum_{M=0}^N \frac{N!}{M!(N-M)!} = 2^N = 2^{10^{24}} \quad (12-19)$$

The binomial formula, $(x+y)^N = \sum_{M=0}^N [N!/M!(N-M)!] x^{N-M} y^M$, is used in the above equation. Substitution of $x=y=1$ yields 2^N , $\omega(M, N-M)$ is the corresponding binomial factor.

(3) Maximum Thermodynamic Probability ω_{\max} of the Most Probable Distribution. The binomial factor is a maximum when $M=N/2$,

$$\omega_{\max} = \frac{N!}{(N/2)!(N/2)!} = \sqrt{\frac{2}{\pi N}} \cdot 2^N \quad (12-20)$$

The Stirling approximate formula ^① $N! = (N/e)^N (2\pi N)^{1/2}$ is used in derivation.

(4) Maximum Probability P_{\max} of the Most Probable Distribution.

$$P_{\max} = \omega_{\max} / \Omega = \sqrt{2/(\pi N)} = \sqrt{2/(10^{24} \pi)} \approx 8 \times 10^{-13} \quad (12-21)$$

Although the probability of the appearance of the most probable distribution is a maximum, the value is very small, only $1/10^{12}$. Why do we still say that the most probable distribution represents all the possible distributions?

(5) Consider the Fluctuation of the Number of Particles. In fact, the numbers of balls in the compartments *A* and *B* are fluctuated with different distributions. However, in the case of a large number of particles for example $N=1 \times 10^{24}$, the difference of several balls in the two compartments can not be detected completely on the macroscopic level; even the difference reaching 10^{12} , compared with 10^{24} is still negligible. The distributions in this range are essentially the same as the most probable distribution with exactly 0.5×10^{24} balls in each compartment of *A* and *B*. The situation will be clear when we sum up those distributions. Calculations show that the sum of the probabilities of those distributions in the range of $0.5 \times 10^{24} \pm 2 \times 10^{12}$ balls in *A* and *B* is virtually 1 (>0.9999). The so called that the most probable distribution can represent all the possible distributions is just directed against systems composed of a large number of particles and is recognized in terms of the consideration of the fluctuation.

Corollary For systems composed of a large amount of particles, the logarithm of the thermodynamic probability of a macroscopic state $\ln \Omega$ can be replaced by that of the most probable distribution $\ln \omega_{\max}$. Still using the above example, $\omega_{\max} / \Omega \approx 1/10^{12}$, $\ln \omega_{\max} = \ln \Omega - \ln 10^{12} = \ln \Omega - 27.6$, because $\Omega = 2^{10^{24}}$, $\ln \Omega = 0.693 \times 10^{24}$, compared with it, 27.6 is a very small number to be neglected. Although ω_{\max} and Ω are notably different, after taking logarithms, $\ln \omega_{\max}$ and $\ln \Omega$ are essentially equal to each other.

5. Maximum-Term Method

^①The series $N! = (N/e)^N (2\pi N)^{1/2} [1 + 1/(12N) + 1/(288N^2) + \dots]$ named after Stirling *J* is not a [convergent series](#). For a certain *N*, there is an optimized truncation correspondingly. For larger *N*, truncated at the first term is accurate enough resulting in the above approximate formula.

The maximum-term method is a method using $\ln \omega_{\max}$ to replace $\ln \Omega$ in derivation. It greatly simplifies the studies in statistical mechanics.

II. Statistical Distributions of Independent-Particle Systems

12.5 Maxwell-Boltzmann Distribution

1. Three Most Probable Distributions for the Independent-Particle Systems

(1) **Maxwell-Boltzmann Distribution (MB)** The distribution named after Maxwell J C and Boltzmann L E can be used for the independent-particle systems composed of classical particles. The particles are distinguishable and energies of them can change continuously.

(2) **Bose-Einstein Distribution (BE)** The distribution named after Bose S N and Einstein A can be used for the independent-particle systems composed of particles with symmetric wave functions and with no restriction for the number of particles occupying each quantum state. Particles observe the principle of identical character of the quantum mechanics and can not be distinguished each other. The exchange for the states of any pair of particles does not change the microscopic state of the whole system. The energy of a particle is quantized and can not be changed continuously.

(3) **Fermi-Dirac Distribution (FD)** The distribution named after Fermi E and Dirac P A can be used for the independent-particle systems composed of particles with anti-symmetric wave functions observing the Pauli exclusive principle that each quantum state can be occupied with only one particle. Besides this, the features are the same as that of the BE distribution.

Arrangement in This Section For the classical statistics and the quantum statistics, there is no difference between them in terms of the statistical principles, the difference lies in the mechanical models adopted. For the ordinary chemical and chemical engineering problems, MB distribution can provide accurate enough results. In this section, the MB

distribution is therefore the main content but with two revisions. Firstly, the quantum statistical method is adopted for derivation where the energies of the particles are considered as quantized, and the results derived are basically the same as those derived by the classical statistical method. Secondly, an approximate revision is given for the identical character (non-distinguishable) of particles. In ordinary conditions, the results after revision are consistent with those obtained by the BE and the FD distributions.

2. Derive the Maxwell-Boltzmann Distribution

(1) **The Main Content of the Derivation Is to Find the Most Probable Distribution.** This is a problem of conditional extremum.

Thermodynamic Probabilities of Distributions For the distribution in terms of the energy levels shown in Eq.(12-10), if the particles are distinguishable, Eq.(12-15) has given $\omega = N! \prod_i (g_i^{N_i} / N_i!)$. After taking logarithm,

$$\ln \omega = \ln N! + \sum_i N_i \ln g_i - \sum_i \ln N_i! \quad (12-22)$$

Because N_i is a large number, substitution of the another Stirling approximate formula^②, $\ln N! = N \ln N - N$, yields

$$\begin{aligned} \ln \omega &= N \ln N - N + \sum_i N_i \ln g_i - \sum_i (N_i \ln N_i - N_i) \\ &= N \ln N - N + \sum_i N_i (1 + \ln (g_i / N_i)) \end{aligned} \quad (12-23)$$

Thermodynamic Probability of the Most Probable Distribution Is a Maximum

In this case, $\delta \ln \omega$, the differential change of $\ln \omega$, should be zero. (Note: $\ln \omega$ is a functional of the energy function ε_i or $\varepsilon(i)$, to be precise, $\delta \ln \omega$ is a functional differential.) Since N is fixed, the differential change δN is zero. From the above equation,

$$\delta \ln \omega = \sum_i \left(\delta N_i + \ln \frac{g_i}{N_i} \delta N_i - N_i \delta \ln N_i \right) = \sum_i \ln \frac{g_i}{N_i} \delta N_i = 0 \quad (12-24)$$

where δN_i is the differential change of the number of particles on the energy level i .

^② When $N > 100$, the formula $N! = (N/e)^N (2\pi N)^{1/2}$ can be further simplified after taking logarithm. Because $\ln(2\pi N)^{1/2}$ is much smaller than $\ln(N/e)^N$ and can be neglected, the formula obtained $\ln N! = \ln(N/e)^N = N \ln N - N$ is also called the Stirling approximate formula.

Constraints In using Eq.(12-24) to find the extremum, it should be noted that these differential changes of the number of particles δN_i are subject to two constraints, the conservation of the number of particles and the conservation of energy.

$$N = \sum_i N_i, \quad \delta N = \sum_i \delta N_i = 0 \quad (12-25)$$

$$E = \sum_i \varepsilon_i N_i, \quad \delta E = \sum_i \varepsilon_i \delta N_i = 0 \quad (12-26)$$

Therefore, the derivation is a problem of finding conditional extremum.

(2) Lagrange Multiplier Method The point of the method named after Lagrange T L is: To find the conditional extremum, adopting multipliers α and β undetermined to multiply Eq.(12-25) and Eq.(12-26), respectively, then subtracting them from the main equation, Eq.(12-24),

$$\sum_i (\ln(g_i/N_i) - \alpha - \beta \varepsilon_i) \delta N_i = 0 \quad (12-27)$$

Originally, due to the two constraints Eq.(12-25) and Eq.(12-26), in all those differential changes of the number of particles on various energy levels δN_i ($i=0, 1, 2, 3 \dots$), two of them are not independent. For example, taking δN_0 and δN_1 as dependent changes, all the others $\delta N_2, \delta N_3, \delta N_4 \dots$ still can change independently, their corresponding factors in Eq.(12-27) should be zero. Now we have two undetermined multipliers α and β in Eq.(12-27), we can select suitable values for them to make the factors of δN_0 and δN_1 also equal zero. Then, we can write for every energy level i :

$$\ln(g_i/N_i) - \alpha - \beta \varepsilon_i = 0, \quad i = 0, 1, 2, 3, \dots \quad (12-28)$$

Using Eq.(12-28) for all the energy levels, accompanying two constraints Eqs.(12-25, 12-26), the number of molecules N_i ($i = 0, 1, 2 \dots$) for every energy level and the two undetermined multiplier can be solved. The result is the most probable distribution with maximum thermodynamic probability subject to the constraints of Eqs.(12-25, 12-26).

(3) Undetermined Multiplier α and β Rewrite Eq.(12-28) as

$$N_i = g_i e^{-\alpha} e^{-\beta \varepsilon_i} \quad (12-29)$$

Substituting into Eq.(12-25), α is solved,

$$N = \sum_i N_i = e^{-\alpha} \sum_i g_i e^{-\beta \varepsilon_i} \quad (12-30)$$

$$e^{-\alpha} = N / \sum_i g_i e^{-\beta \varepsilon_i} \quad (12-31)$$

Substituting into Eq. (12-26) again, β can be solved in principle,

$$E = \sum_i N_i \varepsilon_i = N \frac{\sum_i g_i \varepsilon_i e^{-\beta \varepsilon_i}}{\sum_i g_i e^{-\beta \varepsilon_i}} \quad (12-32)$$

But the energy E of a specific system should be provided. Later we will prove via an ideal gas that

$$\beta = 1/kT \quad (12-33)$$

k is the Boltzmann constant, $k = 13.80658 \times 10^{-24} \text{J} \cdot \text{K}^{-1}$.

(4) **Maxwell-Boltzmann Distribution** Substituting α and β of Eqs.(12-31, 12-33) back into Eq.(12-29), the number of particles N_i on the energy level i for the most probable distribution is obtained. The relation of N_i with the energy ε_i of the energy level and the degeneracy g_i is

$$N_i = \frac{N g_i e^{-\varepsilon_i/kT}}{\sum_i g_i e^{-\varepsilon_i/kT}} = \frac{N g_i e^{-\varepsilon_i/kT}}{q} \quad (12-34)$$

$$P_i = \frac{N_i}{N} = \frac{g_i e^{-\varepsilon_i/kT}}{q} \quad (12-35)$$

where

$$q = \sum_i g_i e^{-\varepsilon_i/kT} \quad (12-36)$$

is called the **molecular partition function**, \sum_i is a summation for all the energy levels (here i is a local variable). $P_i = N_i/N$, is the probability of finding particles on the energy level i . $e^{-\varepsilon_i/kT}$ is called the Boltzmann factor. Eqs.(12-34, 12-35) are the Maxwell-Boltzmann distribution. It adopts a form of distribution in terms of energy levels. The distribution is suitable for the independent-particle systems composed of classical particles but with quantized energies.

(5) **Implications of the MB Distribution** For a certain macroscopic state, the particle distribution in terms of energy levels follows: The lower the energy lever and the larger Boltzmann factor, the larger the degeneracy, the higher probability of finding particles in that energy level will be.

(6) Distributions in terms of Energy Levels and of Quantum States

Besides being in terms of energy levels, the MB distribution can also adopt a form of distribution in terms of quantum states as follows,

$$P_h = \frac{N_h}{N} = \frac{e^{-\varepsilon_h/kT}}{\sum_h e^{-\varepsilon_h/kT}} = \frac{e^{-\varepsilon_h/kT}}{q} \quad (12-37)$$

$P_h = N_h/N$, is the probability of finding particles on the quantum state h . Different from Eq.(12-35), ε_h in Eq.(12-37) is the energy of the quantum

state h , \sum_h is a summation for all the quantum states (here h is a local variable), Because the quantum state is irrelevant to the concept of degeneracy, therefore, g does not appear in the equation. Correspondingly, the molecular partition function should be

$$q = \sum_h e^{-\epsilon_h/kT} \quad (12-38)$$

For a system, $q = \sum_i g_i e^{-\epsilon_i/kT} = \sum_h e^{-\epsilon_h/kT}$, the results of the two forms of q are equivalent. In terms of energy levels and of quantum states are only two different approaches, they reach the same goal.

3. Revision for the Identical Character of Particles

Systems Composed of Independent Localized Particles Take crystals as example, the particles (molecules, atoms or ions) of them are fixed on a certain positions. Because the lattice points are distinguishable, as if the particles fixed on the lattice points are labeled by distinguishable signs. Therefore, the revision for the identical character is not needed. The above results can be used directly.

Systems Composed of Independent Non-Localized Particles Taking ideal gases for example, the molecules of them are identical and non-distinguishable, exchange of any pair of molecules does not create a new microscopic state. But in the above derivation of the MB distribution, all the particles are distinguishable, in this case, strictly we should adopt the BE or the FD distributions. Is it possible to have the same effectiveness by introducing revisions on the basis of the MB distribution? Roughly it seems simple, because the total number of ways for the exchange of N non-localized particles is just the total permutation number $N!$. Divided by $N!$, the revision could be simply completed. However, this exchange has included that of the non-localized particles within the same quantum state which does not create new microscopic state as has been already considered in the derivation of Eq.(12-15). Therefore, simply divided by $N!$ will cause excessive revision.

(Note: The number of ways of lining up N distinguishable bodies as a column in terms of different sequences is called the total permutation number, $A_N = N!$.)

An Approximate Revision for the Thermodynamic Probabilities of

the Non-Localized-Particle Systems When the temperature is not too low, more molecules will occupy the higher energy levels. For the higher translational energy levels, $n_x^2 + n_y^2 + n_z^2$ has larger values in terms of Eq.(12-2), the ranges of the changes of the translational quantum numbers n_x, n_y, n_z are wider, the number of the combinations of n_x, n_y, n_z is very large leading to a very high g . For the higher rotational energy levels, the rotational quantum number J is also large leading to a very high $g_r=2J+1$. On the other hand, when the density is not too high (higher V) and the mass of the non-local particles is not too small, the spacing of the translational energy levels will be very small leading to more particles occupying the higher energy levels. In this case, the degeneracy of almost every energy level is notably greater than the number of particles occupied in this energy level, $g_i \gg N_i$. On this occasion, we can consider that almost every non-local particle occupies a different quantum state. The exchange of N non-localized particles will not include that of particles within the same quantum state. Divided by $N!$ is then quite reasonable. Therefore, when the temperature is not too low, the density is not too high and the mass of particles is not too small, the approximate revision for the identical character of particles for non-localized-particle systems can be realized by simply divided by $N!$ in Eqs.(12-15, 12-16) for the thermodynamic probabilities of distributions and macroscopic states. Correspondingly, we obtain

$$\omega = \prod_i g_i^{N_i} / N_i! \quad (12-39)$$

$$\Omega = \sum_{x(N,E,V)} \omega_x = \sum_{x(N,E,V)} \left(\prod_i g_i^{N_i} / N_i! \right)_x \quad (12-40)$$

When using Ω to derive properties for the non-localized-particle systems, the results will be different from those for the localized-particle systems.

The Most Probable Distribution of the Non-Localized-Particle Systems Will Not Be Changed by the Approximate Revision Due to the conservation of N , the term relevant to $\ln N!$ disappears after taking differentiation. The distribution obtained is then exactly the same as the MB distribution, Eqs.(12-35~12.38) can still be used. The same as the localized-particle systems, the non-localized-particle systems can also adopt the MB distribution but approximately.

4. Bose-Einstein Distribution and Fermi-Dirac Distribution

Boson and Fermion In some occasions, the identical character should be treated strictly. For photons and π mesons with zero or integer spin, they are called the bosons, the BE distribution should be used. For electrons, protons, neutrons, μ mesons and superons with half odd spin, they are called the fermions, the FD distribution should be adopted. The following we write their thermodynamic probabilities of distribution and the distributions in terms of the energy levels:

$$\text{BE Distribution} \quad \omega = \prod_i \frac{(N_i + g_i - 1)!}{N_i! (g_i - 1)!} \quad (12-41)$$

$$N_i = \frac{g_i}{e^\alpha e^{\beta \varepsilon_i} - 1} \quad (12-42)$$

$$\text{FD Distribution} \quad \omega = \prod_i \frac{g_i!}{N_i! (g_i - N_i)!} \quad (12-43)$$

$$N_i = \frac{g_i}{e^\alpha e^{\beta \varepsilon_i} + 1} \quad (12-44)$$

Comparison with the MB Distribution Comparing Eq.(12-29) of the MB distribution, $N_i = g_i e^{-\alpha} e^{-\beta \varepsilon_i}$, with Eq.(12-42) of the BE distribution and Eq.(12-44) of the FD distribution, the phenomenological differences are -1 and $+1$, respectively in the denominators. According to Eqs.(12-31, 12-36), $e^{-\alpha} = N/q$. It will be clear later when we discuss further the molecular partition functions that if the temperature is not too low, the density is not too high and the mass of particles is not too small, $q \gg N$, $e^\alpha \gg 1$. On this occasion, -1 in Eq.(12-42) and $+1$ in Eq.(12-44) can be neglected, the BE distribution and the FD distribution both turn to the MB distribution.

Example 1 Suppose that HCl can be considered as a linear rigid rotator. Calculate the molecular distribution in terms of the rotational energy levels at 300K.

Solution: The relation between the rotational energy level ε_r and the quantum number J for a linear rigid rotator is shown by Eq.(12-3),

$$\varepsilon_r = J(J+1)h^2 / (8\pi^2 I), \quad J=0, 1, 2, \dots, \quad \text{the degeneracy} \quad g_r = 2J+1$$

Substituting into Eq.(12-34), when $J=0$, $g_0=1$, $\varepsilon_0=0$, therefore,

$$N_0 = N / \sum g_r e^{-\varepsilon_r / kT}, \quad N_J = N(2J+1) e^{-\varepsilon_J / kT} / \sum g_r e^{-\varepsilon_r / kT}$$

$$N_J / N_0 = (2J+1) e^{-\varepsilon_J / kT} = (2J+1) \exp[-J(J+1)h^2 / (8\pi^2 I kT)] \quad (12-45)$$

It is known that

$$I_{\text{HCl}} = 26.4 \times 10^{-48} \text{ kg} \cdot \text{m}^2, \quad h = 0.66260755 \times 10^{-33} \text{ J} \cdot \text{s}, \quad k = 13.80658 \times 10^{-24} \text{ J} \cdot \text{K}^{-1}$$

Substituting into the above equation, for $J=1, 3, 6$, we obtain respectively,

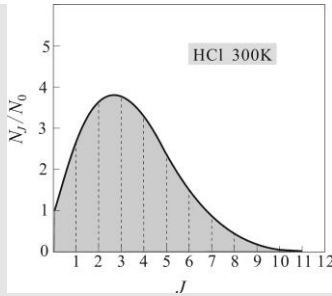
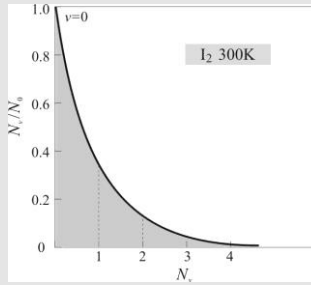


Figure 12-4 Distribution of HCl molecules in terms of rotational energy levels.


 Figure 12-5 Distribution of I₂ molecules in terms of vibrational energy levels.

$$\begin{aligned} N_1/N_0 &= 3 \times \exp[-2 \times (0.6626 \times 10^{-33})^2 / (8\pi^2 \times 26.4 \times 10^{-48} \times 13.81 \times 10^{-24} \times 300)] \\ &= 3 \times \exp(-2 \times 0.05084) = 2.71 \end{aligned}$$

$$N_3/N_0 = 7 \times \exp(-12 \times 0.05084) = 3.80$$

$$N_6/N_0 = 13 \times \exp(-42 \times 0.05084) = 1.54$$

Eq.(12-3) and $g_r = 2J+1$ show that g_r and ϵ_r both increase with J . However, the increase of ϵ_r lowers $e^{-\epsilon_r/(kT)}$, therefore, N_J will exhibit a maximum. The above and more calculation results are depicted in Figure 12-4 showing the molecular distribution of HCl in terms of rotational energy levels at 300K where the ordinate is the relative number of molecules N_J/N_0 distributed on the energy level with a rotational quantum number J . The largest number of molecules appears on the energy level with $J=3$.

Example 2 Suppose that I₂ can be considered as a one-dimensional simple harmonic oscillator. Calculate the molecular distribution of I₂ vapor in terms of the vibrational energy levels.

Solution: The relation between the vibrational energy level ϵ_v and the quantum number v for a one-dimensional simple harmonic oscillator is shown by Eq.(12-4),

$$\epsilon_v = (v + 1/2)h\nu, \quad v = 0, 1, 2, \dots, \quad \text{the degeneracy } g_v = 1$$

For I₂, $\nu = 6.434 \times 10^{12} \text{ s}^{-1}$. Substituting into Eq.(12-34),

$$N_v/N_0 = e^{-(\epsilon_v - \epsilon_0)/kT} = e^{-v h \nu / kT} \quad (12-46)$$

When $v=1$,

$$\frac{N_1}{N_0} = \exp\left(-\frac{1 \times 0.6626 \times 10^{-33} \times 6.434 \times 10^{12}}{13.81 \times 10^{-24} \times 300}\right) = 0.357$$

When v increases from zero, ϵ_v increases correspondingly, $e^{-\epsilon_v/(kT)}$ and N_v decrease monotonically and exponentially. Figure 12-5 depicts the calculation results showing the molecular distribution of I₂ in terms of the vibrational energy levels at 300K where the ordinate is the relative number of molecules N_v/N_0 distributed on the energy level with a vibrational quantum number v . The Figure shows that the majority of molecules are occupied on the ground state.

12.6 Molecular Partition Function

1. Expressions for the Molecular Partition Function

$$q = \sum_i g_i e^{-\epsilon_i/kT} = \sum_h e^{-\epsilon_h/kT}$$

or
$$q_0 = \sum_i g_i e^{-(\varepsilon_i - \varepsilon_0)/kT} \quad (12-47)$$

The former is just Eq.(12-36) and Eq.(12-38). The latter is because that the ground state energy level ε_0 of some particles is not zero, subtracting ε_0 for various energy levels, the zero point of the energy scale is then set on the ground state energy level leading to a simplified treatment. The features of q_0 will be discussed later. q_0 does not equal q , they have the following relation,

$$q = q_0 e^{-\varepsilon_0/kT} \quad (12-48)$$

2. Factorial Characteristics of the Molecular Partition Functions

If neglecting the interactions among the degrees of freedom of various motions, the energy of a molecule is then the summation of the energies of various forms of motions and the degeneracy is the product of the degeneracy of various energy levels. According to Eqs.(12-5, 12-6),

$$\varepsilon = \varepsilon_t + \varepsilon_r + \varepsilon_v + \varepsilon_e + \varepsilon_n, \quad g = g_t \cdot g_r \cdot g_v \cdot g_e \cdot g_n$$

Substitution of them into the molecular partition function, Eq.(12-26), yields

$$\begin{aligned} q &= \sum_{i_t, i_r, i_v, i_e, i_n} g_{t, i_t} g_{r, i_r} g_{v, i_v} g_{e, i_e} g_{n, i_n} \exp[-(\varepsilon_{t, i_t} + \varepsilon_{r, i_r} + \varepsilon_{v, i_v} + \varepsilon_{e, i_e} + \varepsilon_{n, i_n})/kT] \\ &= \sum_i g_{t, i} \exp(-\varepsilon_{t, i}/kT) \sum_i g_{r, i} \exp(-\varepsilon_{r, i}/kT) \sum_i g_{v, i} \exp(-\varepsilon_{v, i}/kT) \\ &\quad \sum_i g_{e, i} \exp(-\varepsilon_{e, i}/kT) \sum_i g_{n, i} \exp(-\varepsilon_{n, i}/kT) = q_t q_r q_v q_e q_n \quad (12-49) \end{aligned}$$

The serial number i is a local variable. From this equation, the molecular partition function (total) of a molecule can then be expressed by multiplying together the molecular partition functions of various forms of motions. This is called the factorial characteristics.

3. Translational Partition Function

Derivation It is convenient to use Eq.(12-38), the distribution in terms of the quantum states in derivation. Remember that the undetermined multiplier β is remained to be solved, therefore, rewrite Eq.(12-38) as $q_h = \sum_h e^{-\beta \varepsilon_h}$ with an unknown β . Substituting Eq.(12-1) into it, the three-dimensional translational partition function q_t is obtained,

$$\begin{aligned} q_t &= \sum_{(n_x, n_y, n_z)} e^{-\beta \varepsilon_t(n_x, n_y, n_z)} = \sum_{(n_x, n_y, n_z)} \exp \left[\frac{-\beta h^2}{8m} \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right) \right] \\ &= \sum_{n_x=1}^{\infty} \exp \left(\frac{-\beta h^2 n_x^2}{8m l_x^2} \right) \sum_{n_y=1}^{\infty} \exp \left(\frac{-\beta h^2 n_y^2}{8m l_y^2} \right) \sum_{n_z=1}^{\infty} \exp \left(\frac{-\beta h^2 n_z^2}{8m l_z^2} \right) \quad (12-50) \end{aligned}$$

As is mentioned before, the summation in the equation can be replaced by integration. Taking the first term for example, let $\beta h^2/8ml_x^2 = a^2$, when $a^2 \ll 1$,

$$\sum_{n_x=1}^{\infty} \exp\left(-\frac{\beta h^2 n_x^2}{8ml_x^2}\right) = \sum_{n_x=1}^{\infty} e^{-a^2 n_x^2} \approx \int_0^{\infty} e^{-a^2 n_x^2} dn_x = \frac{\sqrt{\pi}}{2a} = l_x \left(\frac{2\pi m}{\beta h^2}\right)^{1/2} \quad (12-51)$$

$$\text{So} \quad q_t = l_x l_y l_z \left(\frac{2\pi m}{\beta h^2}\right)^{3/2} = V \left(\frac{2\pi m}{\beta h^2}\right)^{3/2} \quad (12-52)$$

Determine β Combining the condition of the conservation of energy, Eq.(12-26), $E_t = \sum_h \varepsilon_{t,h} N_h$, the distribution in terms of the quantum states, Eq.(12-37), $N_h = N e^{-\varepsilon_{t,h}/(kT)} / q_t$ and Eq.(12-52), also using the relation

$$-(\partial q_t / \partial \beta)_V = \sum_h \varepsilon_{t,h} e^{-\beta \varepsilon_{t,h}},$$

the energy of a three-dimensional translational particle can be derived,

$$E_t = \sum_h N_h \varepsilon_{t,h} = \frac{\sum_h N_h \varepsilon_{t,h} e^{-\beta \varepsilon_{t,h}}}{q_t} = -\frac{N}{q_t} \left(\frac{\partial q_t}{\partial \beta}\right)_V = -N \left(\frac{\partial \ln q_t}{\partial \beta}\right)_V = \frac{3N}{2\beta} \quad (12-53)$$

The subscript V introduced in the partial derivatives is due to the volume dependence of the translational energy levels, referring to Eq.(12-1). We have elucidated that the determination of β needs the energy of a concrete system. Here we adopt an ideal gas composed of N mono-atomic molecules and its energy has been given by the kinetic theory,

$$E = E_t = 3NkT/2 \quad (12-54)$$

k is the Boltzmann constant. Combining Eq.(12-53) and Eq.(12-54), we obtain Eq.(12-33) mentioned before, $\beta = 1/kT$.

Expression of the Translational Partition Function Substitution of β into Eq.(12-52) yields

$$q_t = V \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \quad (12-55)$$

The equation shows that q_t is proportional to the volume of the system then to the amount of substance.

Example 1 At a pressure of $1.013 \times 10^5 \text{ Pa}$ and a temperature of 298 K , calculate the translational partition function for 1 mol of N_2 .

Solution: Molecular mass of N_2 is $m = 46.5 \times 10^{-27} \text{ kg}$. At the above condition, N_2 can be considered as an ideal gas with a volume of

$$V = nRT/p = [1 \times 8.3145 \times 298 / (1.013 \cdot 10^5)] \text{m}^3 = 0.0245 \text{m}^3$$

Substitution into Eq.(12-55) yields

$$q_t = V(2\pi mkT/h^2)^{3/2} = 0.0245 [2\pi \times 46.5 \times 10^{-27} \times 13.81 \times 10^{-24} \times 298 / (0.6626 \times 10^{-33})^2]^{3/2} = 3.51 \times 10^{30}$$

4. Rotational Partition Function

Diatomic Molecules or Linear Many-Atom Molecules

They can

be considered as linear rigid rotator. Substituting Eq.(12-3) into Eq.(12-36), the rotational partition function of linear molecules is obtained,

$$\begin{aligned} q_r &= \sum_i g_{r,i} e^{-\epsilon_{r,i}/kT} = \sum_{J=0}^{\infty} (2J+1) e^{-J(J+1)h^2/8\pi^2 IkT} \\ &= \sum_{J=0}^{\infty} (2J+1) e^{-J(J+1)\Theta_r/T} \end{aligned} \quad (12-56)$$

In the expression of the rotational partition function q_r , the characteristic constant $\Theta_r = h^2/8\pi^2 Ik$ is called the **rotational temperature** relevant to the moment of inertia. At ambient temperature, for ordinary linear molecules, $\Theta_r/T \ll 1$, therefore, the summation in Eq.(12-56) can be replaced by integration. Let $x = J(J+1)$, $dx = (2J+1)dJ$,

$$q_r = \int_0^{\infty} (2J+1) e^{-J(J+1)\Theta_r/T} dJ = \int_0^{\infty} e^{-x\Theta_r/T} dx = T/\Theta_r \quad (12-57)$$

Further we should consider the **symmetry number** σ , it is the number of the same configurations appeared when the molecule rotates one cycle around its symmetry axis. For symmetrical linear molecules, $\sigma=2$, for non-symmetrical molecules, $\sigma=1$. Introducing σ , Eq.(12-57) is revised as:

$$q_r = T/\sigma\Theta_r \quad (12-58)$$

Non-Linear Many-Atom Molecules

They can be considered as

three-dimensional rigid rotator. The rotational partition function is:

$$q_r = \frac{\sqrt{\pi}(8\pi^2 kT)^{3/2}}{\sigma h^3} (I_A I_B I_C)^{1/2} = \frac{\sqrt{\pi}}{\sigma} \left(\frac{T^3}{\Theta_{rA} \Theta_{rB} \Theta_{rC}} \right)^{1/2} \quad (12-59)$$

where I_A , I_B and I_C are three principle moments of inertia, Θ_{rA} , Θ_{rB} and Θ_{rC} are the corresponding three rotational temperatures. They can be obtained by the experimental spectroscopic data or by the quantum mechanical theories.

Table 12-1 lists the symmetry numbers and the rotational temperatures for various linear or non-linear molecules.

Example 2 Calculate the rotational partition function for N_2 at 298K.

Solution: N_2 molecule is homo-nuclear and diatomic, $\sigma=2$. From Table 12-1, $\Theta_r=2.89$ K. Substitution into Eq. (12-58) yields

$$q_r = T/\sigma\Theta_r = 298/(2 \times 2.89) = 51.6$$

5. Vibrational Partition Function

Diatomic Molecules They can be considered as a one-dimensional simple harmonic oscillator. Substitution of Eq.(12-4) into Eq.(12-36) yields

$$\begin{aligned} q_v &= \sum_i g_{v,i} e^{-\epsilon_{v,i}/kT} = \sum_{v=0}^{\infty} e^{-(v+1/2)h\nu/kT} = e^{-\Theta_v/2T} \sum_{v=0}^{\infty} e^{-v\Theta_v/T} \\ &= e^{-\Theta_v/2T} (1 + e^{-\Theta_v/T} + e^{-2\Theta_v/T} + \dots) = \frac{e^{-\Theta_v/2T}}{1 - e^{-\Theta_v/T}} \end{aligned} \quad (12-60)$$

In derivation, the series $1 + x + x^2 + \dots = 1/(1-x)$ is applied. In the expression of the vibrational partition function q_v , the characteristic constant

Table 12-1 Symmetric numbers and rotational temperatures for some gases

Gas	σ	Θ_r /K	Gas	σ	Θ_r /K		
H ₂	2	87.5	CO ₂	2	0.660		
D ₂	2	43.8	CS ₂	2	0.0643		
N ₂	2	2.89	N ₂ O	1	0.610		
O ₂	2	2.08	Gas	σ	Θ_{rA} /K	Θ_{rB} /K	Θ_{rC} /K
Cl ₂	2	0.351	(non-linear)				
Br ₂	2	0.116	H ₂ O	2	40.4	21.1	13.5
I ₂	2	0.0537	D ₂ O	2	22.49	10.56	6.70
CO	1	2.78	H ₂ S	2	15.10	13.09	6.89
NO	1	2.45	SO ₂	2	3.27	0.55	0.47
HCl	1	15.2	NH ₃	3	14.30	14.30	9.08
HBr	1	12.2	CH ₄	12	7.60	7.60	7.60
HI	1	9.43	CCl ₄	12	0.0826	0.0826	0.0826

Note: Data cited from Tien C L, Lienhard J H, Statistical Thermodynamics, 1979, p.178.

$\Theta_v = h\nu/k$ is called the **vibrational temperature** relevant to the vibration frequency of the molecule. It can be obtained from spectroscopy or theories.

The Other Form Because the energy of the ground state of the

simple harmonic oscillator, the zero point energy, is not zero, the vibrational

Table 12-2 Vibrational temperature for some gases
Number in () is degeneracy. Data source is the same as Table 12-1

Gas	Θ_v / K	Gas	Θ_{v1} / K	Θ_{v2} / K	Θ_{v3} / K	Θ_{v4} / K	Θ_{v5} / K	Θ_{v6} / K
H ₂	6320	CO ₂	954(2)	1890	3360			
N ₂	3390	N ₂ O	850(2)	1840	3200			
O ₂	2278	C ₂ H ₂	911(2)	1044(2)	2820	4690	4830	
CO	3120	H ₂ O	2290	5160	5360			
HCl	4330	NH ₃	1360	2330(2)	4780	4880(2)		
HBr	3820	CH ₄	1870(3)	2180(2)	4170	4320(3)		
I ₂	309	CHCl ₃	374(2)	523	938	1090(2)	1745(2)	4330
NO	2745							

partition function usually adopts the form of Eq.(12-47) with $\varepsilon_{v,0}$ as a basis point. The corresponding partition function is

$$q_{0v} = \sum_i g_{v,i} e^{-(\varepsilon_{v,i} - \varepsilon_{v,0})/kT} = (1 - e^{-\Theta_v/T})^{-1} \quad (12-61)$$

The equation shows that when the temperature is low and $T \ll \Theta_v$, $q_{0v}=1$, in this case, all the molecules occupy the ground energy level. As temperature increases, more and more molecules occupy the excited states, q_{0v} will be far more greater than 1. When $T \gg \Theta_v$, $q_{0v} = q_v = T/\Theta_v$.

Many-Atom Molecules There are $3n-5$ and $3n-6$ vibrational degrees of freedom for linear and non-linear molecules, respectively. They can be considered as $3n-5$ and $3n-6$ one-dimensional simple harmonic oscillators with different frequencies. The vibrational partition function is

$$q_{0v} = \prod_{i=1}^s (1 - e^{-\Theta_{v,i}/T})^{-1} \quad (12-62)$$

where $\Theta_{v,i}$ is the vibrational temperature of the i th simple harmonic oscillator. Table 12-2 lists vibrational temperatures for various gases.

Example 3 Calculate the vibrational partition function for N₂ molecule at 298K.

Solution: From Table 12-2, the vibrational temperature for N₂ is $\Theta_v=3390K$.

$$q_v = e^{-\Theta_v/2T} / (1 - e^{-\Theta_v/T}) = e^{-3390/(2 \times 298)} / (1 - e^{-3390/298}) = 3.39 \times 10^{-3}$$

$$q_{0v} = (1 - e^{-\Theta_v/T})^{-1} = (1 - e^{-3390/298})^{-1} \approx 1.00$$

6. Electronic Partition Function

According to Eq.(12-47), when setting the zero point of the energy scale at the ground state energy level, the electronic partition function is:

$$\begin{aligned} q_{0e} &= \sum_i g_{e,i} e^{-(\varepsilon_{e,i} - \varepsilon_{e,0})/kT} \\ &= g_{e,0} + g_{e,1} e^{-(\varepsilon_{e,1} - \varepsilon_{e,0})/kT} + g_{e,2} e^{-(\varepsilon_{e,2} - \varepsilon_{e,0})/kT} + \dots \end{aligned} \quad (12-63)$$

where $\varepsilon_{e,0}$, $\varepsilon_{e,1}$, $\varepsilon_{e,2}$... are the energies of the ground state, the first, the second ... excited states of electronic energy levels, $g_{e,0}$, $g_{e,1}$, $g_{e,2}$... are the corresponding degeneracy. The equation is applicable at a limited volume^②. However, due to large spacing between the different electronic energy levels, besides a few molecules such as NO, O₂, a very high temperature is needed to excite electrons in molecules. Therefore, usually only the first term in Eq.(12-63) is involved,

$$q_{0e} = g_{e,0} \quad (12-64)$$

In this case, the electronic partition function can be expressed by the degeneracy of the electronic ground state energy level. Besides a few molecules such as NO, O₂, for ordinary saturated molecules, $g_{e,0}=1$.

7. Nuclear Partition Function

Similar to q_{0e} , $q_{0n} = g_{n,0}$, the nuclear partition function can be simply expressed by the degeneracy of the nuclear ground state energy level. Ordinary physical and chemical changes are irrelevant to the nuclear changes, therefore, q_{0n} is usually not considered.

Example 4 Write the partition function q_0 for a diatomic molecule.

Solution: Because $q_{0t} \approx q_t$, $q_{0r} \approx q_r$,

$$q_0 = q_{0t} q_{0r} q_{0v} q_{0e} q_{0n} = V(2\pi mkT/h^2)^{3/2} [T/(\sigma \Theta_r)] (1 - e^{-\Theta_v/T})^{-1} g_{e,0} g_{n,0}$$

8. Properties and Significance of the Molecular Partition Functions

(1) The molecular partition functions reflect the integral character of the distributions of all the particles of the system in terms of the translational, the rotational, the vibrational, the electronic and other energy levels or in terms of various quantum states. The molecular partition function (total) represents the summation of various microscopic states relevant to the macroscopic state of the system; therefore, it is a macroscopic property containing all thermodynamic information. Later we will see that once the total molecular partition function and its dependence with the temperature and the volume are known, all other macroscopic thermodynamic properties can be obtained.

^②Taking H atom for example, the degeneracy $g=n^2$, n is the principle quantum number, referring to 9.9.2(3). Eq.(12-63) is then divergent. If the volume is limited, the size of H atom increases with n , the exclusion effect will make the energy level approaches infinity, the Boltzmann factor quickly approaches zero, and the divergence is avoided.

(2) At the fixed temperature and volume, the molecular partition functions can be calculated by those microscopic molecular characteristic properties such as the molecular mass m , the moment of inertia I (or the rotational temperature Θ_r), the characteristic frequency ν (or the vibrational temperature Θ_v), the energy of the electronic ground state and the degeneracy. Therefore, the molecular partition functions are the ties connecting the microscopic properties and the macroscopic properties of the independent-particle systems.

(3) Besides q_t of the translational, q_r , q_v , q_e , q_n of the rotational, the vibrational, the electronic and the nuclear motions are all irrelevant to the amount of substance, therefore, are intensive properties. q_t and $q=q_tq_rq_vq_eq_n$, the total molecular partition function, are proportional to the volume or the amount of substance of the system, therefore, are extensive properties.

(4) q increases with the increase of temperature, referring to Eqs.(12-55, 12-58, 12-60). The higher the temperature, the easier the excitation of particles, the larger q will be. At the same temperature, q_t is the largest, q_r is the second, q_v is the smallest. q_t is the main contribution to q . As shown in Examples 1, 2, and 3, for 1mol of N_2 at 298K and $0.0245m^3$,

$$q_t=3.51 \times 10^{30}, \quad q_r=51.6, \quad q_v=3.39 \times 10^{-3}, \quad q=q_tq_rq_v=6.14 \times 10^{29}$$

(5) Provided that the temperature is not too low, the density is not too high, the molecular mass is not too small, q will be large, on this occasion, the BE and the FD distributions can be replaced by the MB distribution. The above example shows that $q(\sim 6 \times 10^{29}) \gg N(\sim 10^{24})$.

(6) The molecular partition function is the ratio of the total number of particles of the system N to the number of particles occupying the ground energy level N_0 , $q_0=N/N_0$. Substituting Eq.(12-48) into Eq.(12-35), we obtain another form of the MB distribution,

$$\frac{N_i}{N} = \frac{g_i e^{-(\epsilon_i - \epsilon_0)/kT}}{q_0} \quad (12-65)$$

Because of the fact that the ground state energy levels of the most particles are non-degenerate, $g_0=1$, therefore, for the ground state,

$$N_0/N = 1/q_0 \quad \text{or} \quad q_0 = N/N_0 \quad (12-66)$$

When N particles are all located on the ground state energy level, $q_0=1$, q_0 is

a minimum value. When a part of particles are excited from the ground state energy level to higher energy levels, q_0 will be greater than 1, the more particles excited, the higher q_0 will be.

III. Thermodynamic Properties of Independent-Particle Systems

12.7 Thermodynamic Functions of Independent-Particle Systems

1. Energy of the Independent-Particle Systems

Statistical Average According to the second fundamental postulate, a macroscopic mechanical quantity is the statistical average value of the corresponding microscopic quantities. For the energy of an independent-particle system with fixed N , E and V , this topic is exceptionally simple because the constraint of the energy conservation should be satisfied for any one of the microscopic states which have the same energy E . Treating the topic alternatively, in terms of Eq.(12-26),

$$E = \sum_i N_i \varepsilon_i = N \sum_i (N_i / N) \varepsilon_i \quad (12-67)$$

where N_i / N is the probability of finding molecules on the energy level i , $\sum_i (N_i / N) \varepsilon_i$ is the average energy of a molecule, multiplying the number of molecules N , the result is the statistical average of the energy of the system.

Relation between Energy and the Molecular Partition Function

The spacing of the energy levels is relevant to V . When V is fixed, g_i and ε_i are constants, therefore, we have the following formula,

$$\left(\frac{\partial q}{\partial T} \right)_V = \frac{\sum_i \varepsilon_i g_i e^{-\varepsilon_i / kT}}{kT^2}$$

Using this formula, substitution of the MB distribution, Eq.(12-35), into Eq.(12-67) yields

$$E = \frac{N}{q} \sum_i \varepsilon_i g_i e^{-\varepsilon_i / kT} = \frac{NkT^2}{q} \left(\frac{\partial q}{\partial T} \right)_V = NkT^2 \left(\frac{\partial \ln q}{\partial T} \right)_V \quad (12-68)$$

Energy Equipartition Theorem For an independent-particle system composed of N diatomic molecules, if the temperature is high

enough to allow adopting $q_v = T/\Theta_v$ for the vibration but not excessive high to excite the electronic energy level then the electronic motion can be considered as non-thermal movement. Using Eqs.(12-55, 12-58), the partition function of the thermal movements can be expressed as

$$q = q_t q_r q_v = V \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \left(\frac{T}{\sigma \Theta_r} \right) \left(\frac{T}{\Theta_v} \right) \quad (12-69)$$

Substituting into Eq.(12-68), the corresponding energy is obtained,

$$E = NkT^2 \left(\frac{\partial \ln q_t}{\partial T} + \frac{\partial \ln q_r}{\partial T} + \frac{\partial \ln q_v}{\partial T} \right) = \frac{3}{2} NkT + NkT + NkT = \frac{7}{2} NkT \quad (12-70)$$

The equation indicates that the energy of the thermal movements is allocated in terms of the degrees of freedom of the motions of the molecule. Each degree has an energy of $NkT/2$ in principle. For a diatomic molecule, there are 3 translational and 2 rotational degrees of freedom with energies of $3NkT/2$ and NkT , respectively. The special aspect is the vibrational motion with only one degree of freedom while with energy NkT allocated. This can be explained as that different from the translational and the rotational energies, the vibrational energy is composed of two parts, the kinetic energy and the potential energy. Therefore, one degree is given two parts of energies.

2. Entropy of the Independent-Particle Systems

The entropy is a non-mechanical quantity without the corresponding microscopic counterpart. It can be obtained by comparison with the thermodynamic results based on the statistical calculations for the mechanical quantities. There are several ways to realize this comparison. In this section, we first find the relation between the entropy and the distribution in terms of energy levels through the thermodynamic fundamental equations, further obtain the relation between the entropy and the thermodynamic probability, finally, we derive the relation between the entropy and the partition function by applying the MB distribution.

(1) Relation between Entropy and the Distribution in terms of Energy Levels For a homogeneous closed system, according to the thermodynamic fundamental equation, Eq.(2-40), where the thermodynamic energy U is just the energy E in this chapter, we can write

$$dE = TdS - pdV \quad (12-71)$$

Terms TdS and $-pdV$ on the right side are the contributions to the change of E by keeping V unchanged and by changing V , respectively. Examining in terms of the microscopic point of view, according to Eq.(12-67) $E = \sum_i N_i \varepsilon_i$, the differential change of E for an independent-particle system is

$$dE = \sum_i \varepsilon_i dN_i + \sum_i N_i d\varepsilon_i \quad (12-72)$$

The first term on the right side is the energy increment due to the change of the distribution number N_i when the energy level ε_i is fixed, the second term is that due to the change of ε_i when N_i is fixed. According to Eq.(12-2), the spacing of the energy levels is only relevant to V , therefore, these two terms represent the energy exchanged between the system and the surroundings when V is kept unchanged and V is changed. Comparing with Eq.(12-71), it is then clear that the former is just the term TdS , the heat exchange between the system and the surroundings, the latter is the term $-pdV$, the work exchange between the system and the surroundings.

$$\sum_i \varepsilon_i dN_i = TdS = dQ_R \quad (12-73)$$

$$\sum_i N_i d\varepsilon_i = -pdV = dW_R \quad (12-74)$$

Eq.(12-72) can therefore be considered as the **microscopic form of the thermodynamic fundamental equation**. While Eq.(12-73) connects the entropy change and the changes of the numbers of particles on various energy levels that we are most interested in at present.

(2) Relation between Entropy and the Thermodynamic Probability

The following derivation is composed of two steps:

Derive the Relation between $\sum_i \varepsilon_i dN_i$ and $\ln \Omega$ According to Eq.(12-16) for the thermodynamic probability of the macroscopic state of an independent-particle system, and the maximum-term method in 12.4.5, $\ln \Omega$ can be expressed as

$$\ln \Omega = \ln \left[N! \sum_{x(N,E,V)} \left(\prod_i \frac{g_i^{N_i}}{N_i!} \right)_{x(N,E,V)} \right] \approx \ln \omega_{\max} = \ln \left(N! \prod_i \frac{g_i^{N_i}}{N_i!} \right) \quad (12-75)$$

where N_i in the front term is the number of particles on the energy level i for an arbitrary distribution $x(N,E,V)$, while N_i in the tail term is that for the

most probable distribution following the MB distribution. Using $\ln N! = N \ln N - N$,

$$\ln \Omega \approx \ln \omega_{\max} = N \ln N - N + \sum_i (N_i \ln g_i - N_i \ln N_i + N_i) \quad (12-76)$$

Differentiate further and noting that N is constant, $\sum_i dN_i = 0$, we obtain

$$\begin{aligned} d \ln \Omega &= \sum_i d(N_i \ln g_i - N_i \ln N_i + N_i) = \sum_i d(N_i \ln g_i - N_i \ln N_i) \\ &= \sum_i (\ln(g_i / N_i) dN_i - dN_i) = \sum_i \ln(g_i / N_i) dN_i \end{aligned} \quad (12-77)$$

Substitution of the MB distribution, Eq.(12-34), $N_i = N g_i e^{-\varepsilon_i / kT} / q$, yields

$$d \ln \Omega = \ln \frac{q}{N} \sum_i dN_i + \frac{1}{kT} \sum_i \varepsilon_i dN_i = \frac{1}{kT} \sum_i \varepsilon_i dN_i \quad (12-78)$$

If adopting Eq.(12-40) of the independent-localized-particle systems, no $N!$ in the expression of Ω , because of the conservation of N , $\ln N!$ disappears after the differentiation. Therefore, Eq.(12-78) can be used for both the systems composed of independent localized and non-localized particles.

Boltzmann Relation Comparing Eq.(12-73) with Eq.(12-78),

$$dS = k d \ln \Omega \quad , \quad S = k \ln \Omega + C \quad (12-79)$$

where C is an integration constant. Let $S=0$ at $\Omega=1$, then $C=0$, Eq.(12-79) turns to

$$S = k \ln \Omega \quad (12-80)$$

This equation is called the Boltzmann relation which indicates that the more microscopic states possessed by a macroscopic state of the system, or the larger thermodynamic probability, the more chaotic is the system and the larger entropy will be. This shows the physical meaning of the **entropy**, it is **a measure of the chaotic extent of the system**. When $\Omega=1$, only one microscopic state, the system is then the most regular, the chaotic extent is zero and the entropy is zero. This is just the case of $T=0$, as shown by the third law of thermodynamics.

(3) Relation between Entropy and the Molecular Partition Function

Independent-Localized-Particle Systems Substitution of the MB distribution, Eq.(12-34), into Eq.(12-76) yields

$$\begin{aligned} \ln \Omega &\approx \ln \omega_{\max} = N \ln N + \sum_i N_i \ln(q e^{\varepsilon_i / kT} / N) \\ &= N \ln q + \sum_i N_i \varepsilon_i / kT = N \ln q + E / kT \end{aligned} \quad (12-81)$$

Substituting into Eq.(12-80) and using Eq.(12-68),

$$S = Nk \ln q + \frac{E}{T} = Nk \ln q + NkT \left(\frac{\partial \ln q}{\partial T} \right)_V \quad (12-82)$$

Independent-Non-Localized-Particle Systems According to Eq.(12-16) and Eq.(12-40), the thermodynamic probability of the macroscopic state of a non-localized-particle system is $1/N!$ of that of a localized-particle system. Eqs.(12-81, 12-82) change correspondingly to

$$\ln \Omega \approx \ln \omega_{\max} = N \ln(q/N) + E/kT + N \quad (12-83)$$

$$S = Nk \ln \frac{q}{N} + NkT \left(\frac{\partial \ln q}{\partial T} \right)_V + Nk \quad (12-84)$$

Different from the energy expression, there are difference between the entropy expressions of the localized- and the non-localized-particle systems.

3. Relations between the Other Thermodynamic Functions and the Molecular Partition Function for the Independent-Particle Systems

Starting from Eqs.(12-68, 12-82, 12-84) for the relations between the energy, the entropy and q , combining with the definitions (U is replaced by E): $C_V = (\partial E / \partial T)_V$, $A = E - TS$, $p = -(\partial A / \partial V)_T$, $\mu = (\partial A / \partial n)_{T,V}$, $H = E + pV$, $G = A + pV$, the relations can be obtained for other thermodynamic functions, they are listed with E and S together as follows:

$$E = NkT^2 (\partial \ln q / \partial T)_{V,N} \quad (12-68)$$

$$S = Nk \ln q + NkT (\partial \ln q / \partial T)_{V,N} \quad (\text{localized}) \quad (12-82)$$

$$S = Nk \ln(q/N) + NkT (\partial \ln q / \partial T)_{V,N} + Nk \quad (\text{non-localized}) \quad (12-84)$$

$$C_V = (Nk/T^2) [\partial^2 \ln q / \partial (1/T)^2]_V \quad (12-85)$$

$$A = -NkT \ln q \quad (\text{localized}) \quad (12-86)$$

$$A = -NkT \ln(q/N) - NkT \quad (\text{non-localized}) \quad (12-87)$$

$$p = NkT (\partial \ln q / \partial V)_{T,N} \quad (12-88)$$

$$\mu = -LkT \ln q = -LkT \ln q_0 + L\varepsilon_0 \quad (\text{localized}) \quad (12-89)$$

$$\mu = -LkT \ln(q/N) = -LkT \ln(q_0/N) + L\varepsilon_0 \quad (\text{non-localized}) \quad (12-90)$$

$$H = NkT^2 (\partial \ln q / \partial T)_{V,N} + NkT (\partial \ln q / \partial \ln V)_{T,N} \quad (12-91)$$

$$G = -NkT \ln q + NkT (\partial \ln q / \partial \ln V)_{T,N} \quad (\text{localized}) \quad (12-92)$$

$$G = -NkT \ln(q/N) - NkT + NkT (\partial \ln q / \partial \ln V)_{T,N} \quad (\text{non-localized}) \quad (12-93)$$

Ideal-Gas Equation of State Ideal gases can be considered as independent-non-localized-particle systems. Their partition functions of the

internal movements such as the rotational, the vibrational, the electronic and the nuclear partition functions are all irrelevant to the volume V . Substitution of q_t of Eq.(12-55) into Eq.(12-88) yields the ideal-gas equation of state,

$$p = NkT(\partial \ln q_t / \partial V)_{T,N} = NkT d \ln V / dV = NkT/V \quad (12-94)$$

Comparing with Eq.(1-3) $pV = nRT$, $R = Nk/n = Lk$, L is the Avogadro constant.

12.8 Standard Molar Heat Capacity of Gases

The standard state of gases is the ideal-gas state at a pressure of p° . The standard isochoric heat capacity $C_{V,m}^\circ$ can be calculated by Eq.(1-85) and the isobaric one $C_{p,m}^\circ$ by $C_{p,m}^\circ = C_{V,m}^\circ + R$. If the temperature is not too high that the electronic motion can be considered

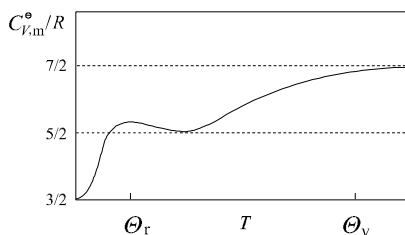


Figure 12-6 A sketch of the temperature dependence of $C_{V,m}^\circ$ for diatomic molecules

as a non-thermal movement, the molecular partition function is then $q = q_t q_r q_v$. Substituting into Eq.(12-85) and noting that $Nk = nR$, we obtain

$$C_{V,m}^\circ = \frac{R}{T^2} \left[\frac{\partial^2 \ln q_t}{\partial (1/T)^2} + \frac{\partial^2 \ln q_r}{\partial (1/T)^2} + \frac{\partial^2 \ln q_v}{\partial (1/T)^2} \right]_V = C_{V,m,t}^\circ + C_{V,m,r}^\circ + C_{V,m,v}^\circ \quad (12-95)$$

$C_{V,m}^\circ$ can be decomposed to the contributions of three forms of motions, the translational, the rotational and the vibrational.

Diatomic Molecules According to Eqs.(12-55, 12-58, 12-60), $q_t = V(2\pi mkT/h^2)^{3/2}$, $q_r = T/\sigma\Theta_r$, $q_v = e^{-\Theta_v/2T}/(1 - e^{-\Theta_v/T})$, substitution into Eq.(12-95) yields

$$C_{V,m,t}^\circ = \frac{R}{T^2} \left[\frac{\partial^2 \ln q_t}{\partial (1/T)^2} \right]_V = \frac{3R}{2} \quad (12-96)$$

$$C_{V,m,r}^\circ = \frac{R}{T^2} \left[\frac{\partial^2 \ln q_r}{\partial (1/T)^2} \right]_V = R \quad (12-97)$$

$$C_{V,m,v}^\circ = \frac{R}{T^2} \left[\frac{\partial^2 \ln q_v}{\partial (1/T)^2} \right]_V = R \left(\frac{\Theta_v}{T} \right)^2 \frac{e^{\Theta_v/T}}{(e^{\Theta_v/T} - 1)^2} \quad (12-98)$$

Figure 12-6 is a sketch of the calculated temperature dependence of $C_{V,m}^\circ$ for

diatomic molecules. It is shown that at very low temperature, $C_{v,m}^{\Theta}$ is near $3R/2$ contributed almost all by the translational motion. With the increasing temperature up to a little bit higher than Θ_r , $C_{v,m}^{\Theta}$ reaches $5R/2$. According to Eq.(12-97), the contribution by the rotational motion is R independent of temperature. The real circumstance is that the rotational motion is gradually excited with the increasing temperature and the curve shows a maximum. This is because in the derivation of Eq.(12-58) for q_r , the classical approximation is adopted to replace the summation by integration. If using strict summation, the curve with a maximum shown in the Figure will be obtained. To keep on increasing temperature, the vibrational motion will be gradually excited. When the temperature exceeds Θ_v notably, the contribution of the vibration approaches R , the total $C_{v,m}^{\Theta}$ approaches $7R/2$.

Many-Atom Molecules For these molecules, the rotation should be considered as a three-dimensional rotator. The vibrational degrees of freedom will be $3n-5$ or $3n-6$, their contributions should be accounted respectively.

Example Prove that when $T \gg \Theta_v$, the contribution of the vibration of a diatomic molecule to the standard molar isochoric heat capacity is R .

Solution: When $\Theta_v/T \ll 1$, $e^{\Theta_v/T} \approx 1 + \Theta_v/T$, substituting into Eq.(12-98),

$$C_{v,m,v}^{\Theta} \approx R(1 + \Theta_v/T) \approx R$$

12.9 Heat Capacity of Crystals

1. Einstein Model

The model was proposed by Einstein A in 1907. The basic points of the model are: (1) The atoms or mono-atomic ions in crystals can only carry out simple harmonic vibrations on the lattice points and the heat capacity is determined completely by the variation of the vibrational energy with temperature. (2) The vibrations of these atoms are independent and irrelevant to each other. (3) All the atoms have the same simple harmonic frequency. The essential of this ideal crystal model is to consider the N atoms of the crystal as N independent three-dimensional simple harmonic oscillators with the same frequency, or $3N$ independent one-dimensional

simple harmonic oscillators with the same frequency.

Expressions for Vibrational Energy and Heat Capacity According to Eq.(12-60), the partition function of a crystal is

$$q = q_v^3 = e^{-3\Theta_v/2T} / (1 - e^{-\Theta_v/T})^3 \quad (12-99)$$

Substituting into Eqs.(12-68, 12-85), the expressions for the vibrational energy and the molar isochoric heat capacity of crystals is obtained,

$$E_v = 3NkT \left[\frac{\Theta_E}{2T} + \frac{\Theta_E/T}{e^{\Theta_E/T} - 1} \right] \quad (12-100)$$

$$C_{V,m} = 3R \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2} \left(\frac{\Theta_E}{T} \right)^2 \quad (12-101)$$

The latter equation is called the **Einstein Equation** for the Heat Capacity of Crystals. $\Theta_E = \Theta_v = h\nu/k$ is called the **Einstein temperature**.

Comparison between Theoretical Predictions and Experimental values

Figure 12-7 shows the comparison between the experimental and the theoretical heat capacities for diamond. Θ_E selected is 1325K. The result is consistent with the experimental fact

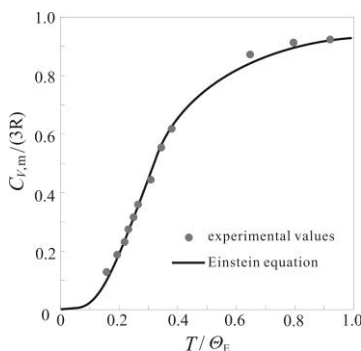


Figure 12-7 Comparison between experiment and theoretical heat capacities for diamond. Cited from: Mandl F, Statistical Physics, 1977, p.157.

that the heat capacity approaches zero with decreasing temperature. However, because of the excessive simplification of the model, the theoretical predictions for $C_{V,m}$ in the low temperature range are a little smaller than the experimental values.

Dulong-Petit Rule The rule says that the heat capacity of various atomic crystals is about $25\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. When the temperature is comparatively high, due to $\Theta_E/T \ll 1$, $e^{\Theta_E/T} \approx 1 + \Theta_E/T$, Eq.(12-101) turns to: $C_{V,m} \approx 3R \approx 25\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, the Einstein theory has predicted this empirical rule.

2. Debye Model

Basic Points of the Model and Expression for Heat Capacity In 1912, Debye P J W revised the Einstein model by considering that the

vibrations of atoms or mono-atomic ions in crystals are not possible to be independent, what happens must be a kind of complex coupled vibration. According to the classical mechanics, this coupled vibration can be decomposed to $3N$ simple harmonic vibrations with different frequencies, the highest limit of the frequencies is called the **Debye frequency** with a symbol ν_D . The revised model is a dependent-particle system. Debye then derived the following expression for the heat capacity,

$$C_{V,m} = 3R \times 3 \left(T / \Theta_D \right)^3 \int_0^{\Theta_D/T} e^x x^4 (e^x - 1)^{-2} dx \quad (12-102)$$

where $x = h\nu/kT$, $\Theta_D = h\nu_D/k$ is called the **Debye temperature**. Compared with experimental result, the Debye equation shows notable improvement than the Einstein equation in the low temperature region. In that region, Eq.(12-102) turns to

$$C_{V,m} = \frac{12}{5} \pi^4 R \left(T / \Theta_D \right)^3 = 1944 \left(T / \Theta_D \right)^3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \quad (12-103)$$

This is the Debye equation in Chapter 1, Eq.(1-39), that must be used to calculate the standard entropy by the third law of thermodynamics. The equation is used for non-metallic solids. For metal crystals, the contribution of the electronic energy levels should be included.

12.10 Standard Molar Entropy of Gases

On the macroscopic level, the entropies of gases are obtained by using the experimental calorimetric data of the heat capacities and the enthalpies of phase transition then carrying the integration from 0K to the temperature studied. Therefore, they are usually called the **third-law entropy** or the **calorimetric entropy**. They are the entropy of the substances relevant to the energy of the molecular thermal movements throughout the whole process of the increasing or decreasing temperature, therefore, are also called the **thermal entropy**. Statistical mechanics can be used to obtain the thermal entropies theoretically from the microscopic properties of substance. Because the microscopic molecular characteristic properties are usually obtained by the spectroscopy, therefore, those entropies are correspondingly called the **statistical entropy** or the **spectroscopic entropy**. When $n=1\text{mol}$ and $p = p^\ominus$, it is the standard molar entropy.

Expressions for Entropy Adopting Eq.(12-84) for the independent non-localized-particle systems at not too high a temperature, the electronic motion can be considered as non-thermal movement, $q=q_t q_r q_v$, $E=E_t+E_r+E_v$, then

$$\begin{aligned} S_t &= Nk \ln(q_t/N) + (E_t/T) + Nk \\ S_r &= Nk \ln q_r + E_r/T \\ S_v &= Nk \ln q_v + E_v/T \\ S &= S_t + S_r + S_v \end{aligned} \quad (12-104)$$

(1) **Translational Entropy** Substituting $q_t = V(2\pi mkT/h^2)^{3/2}$ of Eq.(12-55) and $E_t = NkT^2(\partial \ln q_t / \partial T)_v$ of Eq.(12-68) into Eq.(12-104),

$$S_t = \frac{5}{2} Nk + Nk \ln \left[(2\pi mkT)^{3/2} V h^{-3} N^{-1} \right] \quad (12-105)$$

It is called the **Sackur-Tetrode Equation** for translational entropy.

(2) **Rotational Entropy** Rewrite Eq.(12-68) as $E_r = NkT^2(\partial \ln q_r / \partial T)_v$,

Linear Molecules Substituting $q_r = T/(\sigma \Theta_r)$ of Eq.(12-58) and E_r above into Eq.(12-104), the equation for rotational entropy of linear molecules is obtained,

$$S_r = Nk \left[1 + \ln(T/\sigma \Theta_r) \right] \quad (12-106)$$

Non-Linear Molecules Using q_r of Eq.(12-59), an equation for rotational entropy of non-linear molecules is obtained,

$$S_r = Nk \left\{ \frac{3}{2} + \ln \left[\frac{\sqrt{\pi}}{\sigma} \left(\frac{T^3}{\Theta_{rA} \Theta_{rB} \Theta_{rC}} \right)^{1/2} \right] \right\} \quad (12-107)$$

(3) **Vibrational Entropy** Adopt q_{0v} and E_{0v} , and rewrite Eq.(12-68) as $E_{0v} = NkT^2(\partial \ln q_{0v} / \partial T)_v$.

Diatomic Molecules Substituting $q_{0v} = (1 - e^{-\Theta_v/T})^{-1}$ of Eq.(12-61) and E_{0v} above into Eq.(12-104), the equation for vibrational entropy of diatomic molecules is obtained,

$$S_v = Nk \left[\frac{\Theta_v}{T} \frac{1}{e^{\Theta_v/T} - 1} - \ln(1 - e^{-\Theta_v/T}) \right] \quad (12-108)$$

Many-Atom Molecules Substituting $q_{0v} = \prod_{i=1}^s (1 - e^{-\Theta_{v,i}/T})^{-1}$ of Eq.(12-62) and E_{0v} above into Eq.(12-104), an equation for vibrational entropy of many-atom molecules is obtained,

$$S_v = Nk \sum_i \left[\frac{\Theta_{v,i}}{T} \frac{1}{e^{\Theta_{v,i}/T} - 1} - \ln(1 - e^{-\Theta_{v,i}/T}) \right] \quad (12-109)$$

Example Calculate the standard molar entropy S_m° of gaseous HCl at 298.15K using statistical method.

Solution: $m = [36.45 \times 10^{-3} / (6.022 \times 10^{23})] \text{kg} = 6.053 \times 10^{-26} \text{kg}$ for HCl molecule. The molar volume is $V_m = RT/p = [8.3145 \times 298.15 / (0.1 \cdot 10^6)] \text{m}^3 \cdot \text{mol}^{-1} = 0.02479 \text{m}^3 \cdot \text{mol}^{-1}$ at $p = p^\circ = 0.1 \text{MPa}$ and 298.15K. Substituting into Eq.(12-105),

$$S_{m,t}^\circ = 8.3145 \left[\frac{5}{2} + \ln \frac{(2\pi \times 6.053 \times 10^{-26} \times 13.81 \times 10^{-24} \times 298.15)^{3/2} \times 0.02479}{(0.6626 \times 10^{-33})^3 \times 6.022 \times 10^{23}} \right] \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$= 153.7 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

For HCl molecule, $\Theta_r = 15.2 \text{K}$, $\sigma = 1$, substituting into Eq.(12-106),

$$S_{m,r}^\circ = 8.3145 [1 + \ln(298.15 / (1 \times 15.2))] \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 33.1 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

For HCl molecule, $\Theta_v = 4330 \text{K}$, $\Theta_v/T = 14.52$, substituting into Eq.(12-108),

$$S_{m,v}^\circ = 8.3145 [14.52 \times (e^{14.52} - 1)^{-1} - \ln(1 - e^{-14.52})] \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \approx 0$$

$$S_m^\circ(298.15\text{K}) = S_{m,t}^\circ + S_{m,r}^\circ + S_{m,v}^\circ = (153.7 + 33.1) \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 186.8 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Features of Spectroscopic Entropy The above example shows that the contribution from the translation is the largest, from the rotation is the next, and from the vibration is very small hence usually neglected. It is supposed reasonably that the larger the molecular mass, or the larger moment of inertia and the smaller the symmetry number at the same mass, the larger standard molar entropy of a gas will be.

Comparison between Spectroscopic and Calorimetric Entropies

The comparison is shown in Table 12-3 indicating the consistency between

Table 12-3 Standard molar entropies by statistical mechanics (spectroscopic) and by the third law of thermodynamics (calorimetric), $S_m^\circ(298.15\text{K})/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

Gas	N ₂	O ₂	Cl ₂	HCl	HBr	HI	H ₂ O	N ₂ O	NH ₃	CH ₄	C ₂ H ₄
Stat. mech.	191.5	205.1	223.0	186.8	198.7	206.7	188.7	220.0	192.2	185.6	219.5
Third law	192.0	205.4	223.1	186.2	199.2	207.1	185.3	215.2	192.1	185.4	219.6

Most data are cited from: Rushbrooke G S. Introduction to Statistical Mechanics. 1949

the two kinds of entropies but with a few exceptions. For examples, N₂O and H₂O listed in the Table, and CO, D₂O, H₂, D₂, CH₃D that are not listed, their spectroscopic entropies are larger than the calorimetric entropies.

Reasons of Discrepancies Because the thermal entropy might not be released completely when those gases are cooled from 298.15K to 0K,

after all, a part of the thermal entropy turns to the temperature independent **configurationally entropy** or **residual entropy** remained in the crystals, which leads to the non-zero entropy at 0K. This residual entropy is created when the configurations with a fair number of microscopic states at a higher temperature are preserved at lower temperatures because of the kinetic retardation. For example, N_2O molecule has a non-symmetric linear structure $\text{N}\equiv\text{N}=\text{O}$. At 0K, if it was in a complete equilibrium, a neatly arranged crystal $\text{NNO NNO NNO} \cdots$ would be formed with only one microscopic state, $\Omega=1$, according to Eq.(12-80), $S=k\ln\Omega$, $S_0=0$. However, as the atoms N and O are close neighbor in the periodic table with a very small difference, at lowering the temperature, because of the kinetic obstacles, the solid can not approach orderly arrangement quickly, the random arrangement at the higher temperature is frozen up, leading to a part of the thermal entropy transforming to the temperature independent residual entropy remaining in crystals.

12.11 Standard Equilibrium Constant of Gaseous Reactions

Standard Equilibrium Constant K° Using the standard molar Gibbs function of reaction $\Delta_r G_m^\circ$ for a gaseous reaction $0 = -e\text{E} - f\text{F} + g\text{G} + r\text{R}$ or $0 = \sum_B \nu_B \text{B}$, K° can be expressed according to Eqs.(5-12, 5-19),

$$K^\circ = \exp\left(-\frac{\Delta_r G_m^\circ}{RT}\right) = \exp\left(-\frac{\sum_B \nu_B \mu_B^\circ(\text{g})}{RT}\right) = \lim_{p \rightarrow 0} \prod_B \left(\frac{y_B^{\text{eq}} p}{p^\circ}\right)^{\nu_B} \quad (12-110)$$

where μ_B° is the chemical potential of the component B at standard state (for ideal gas, $p = p^\circ$, $p^\circ = 0.1\text{MPa}$), y_B^{eq} is the mole fraction of the component B at equilibrium.

Relation between K° and the Molecular Partition Function By using $pV = NkT$ and Eq.(12-90), μ_B° at standard state can be expressed as

$$\mu_B^\circ = -LkT \ln \left(\frac{q_{0B}}{N_B} \right)^\circ + L\varepsilon_{0B} = -LkT \ln \frac{q_{0B} kT}{p^\circ V} + L\varepsilon_{0B} \quad (12-111)$$

where q_{0B} is the molecular partition function of B molecule which is dependent on the volume V , while q_{0B}/V is independent of V . Substitution of

this equation into Eq.(12-110) yields

$$\begin{aligned}
 K^\circ &= \exp \left[- \sum_B \left(-v_B \ln(q_{0B} kT / p^\circ V) + v_B L \varepsilon_{0B} / RT \right) \right] \\
 &= \prod_B (q_{0B} kT / p^\circ V)^{v_B} \exp \left(- \sum_B v_B \varepsilon_{0B} / kT \right) \\
 &= \frac{(q_{0G}/V)^g (q_{0R}/V)^r}{(q_{0E}/V)^e (q_{0F}/V)^f} \left(\frac{p^\circ}{kT} \right)^{-\sum_B v_B} \exp \left(- \frac{\Delta \varepsilon_0}{kT} \right) \quad (12-112)
 \end{aligned}$$

where $\Delta \varepsilon_0 = \sum_B v_B \varepsilon_{0B}$. This equation connects the standard equilibrium constant with the molecular partition functions and $\Delta \varepsilon_0$ that can be used to calculate the standard equilibrium constant theoretically by the microscopic molecular characteristic properties.

Applying Factorial Characteristics of the Molecular Partition Functions The molecular partition function q_{0B} can be expressed as

$$q_{0B} = q_{tB} q_{rB} q_{0vB} q_{0eB} q_{0nB} \quad (12-113)$$

Because the ground state energy level of translational motion can be neglected and that of the rotational motion is zero, subscript 0 is not applied for q_{tB} and q_{rB} . Substitution of q_t of Eq.(12-55) yields

$$q_{0B}/V = \left(2\pi m_B kT / h^2 \right)^{3/2} q_{rB} q_{0vB} q_{0eB} q_{0nB} \quad (12-114)$$

For various internal movements, the molecular partition functions can be calculated by equations introduced in 12.6. Eq.(12-114) shows that q_{0B}/V is only relevant to temperature and irrelevant to volume, the standard equilibrium constant calculated is determined by the temperature and the nature of the reaction solely.

Calculation for $\Delta \varepsilon_0$ $\Delta \varepsilon_0$ is the energy difference between the energy levels of reactants and products, $\Delta \varepsilon_0 = g\varepsilon_{0G} + r\varepsilon_{0R} - e\varepsilon_{0E} - f\varepsilon_{0F}$. In calculations, a uniform reference should be selected, which usually takes the ground state energy levels of atoms of the reactants or the products, referring to Figure 12-8 where D_E, D_F, D_G, D_R represent the dissociation energies of molecules of the reactants and the products, respectively. The Figure shows:

$$\begin{aligned}
 \Delta \varepsilon_0 &= (eD_E + fD_F) - (gD_G + rD_R) \\
 &= (e\varepsilon_{0E} + f\varepsilon_{0F}) - (g\varepsilon_{0G} + r\varepsilon_{0R}) \quad (12-115)
 \end{aligned}$$

The dissociation energies of

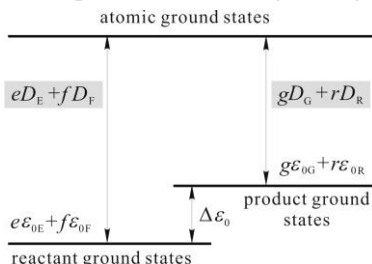


Figure 12-8 Relation between $\Delta \varepsilon_0$ and the dissociation energies of reactants and products.

molecules can be obtained by the experimental spectroscopic data or by the quantum mechanical theories.

Standard Molar Thermodynamic Functions of Reaction Having K° is equivalent to obtaining $\Delta_r G_m^\circ$. Using the relations of reaction thermodynamics, the other standard molar thermodynamic functions of reaction such as $\Delta_r H_m^\circ$ and $\Delta_r S_m^\circ$ can be calculated.

Example Calculate the standard equilibrium constant K° for the gaseous reaction $I_2 \rightleftharpoons 2I$ at 1073K by the data in the Table on the right provided by spectroscopy. From the ground state spectral term of the iodine atom, the degeneracy of I is obtained as $g_{e,0}=4$.

Gas	Θ_r / K	Θ_v / K	$D / \text{kJ} \cdot \text{mol}^{-1}$
I_2	0.0537	309	148.7
I	—	—	—

Solution: According to Eqs.(12-112, 12-115),

$$K^\circ = (q_{0I}/V) \left(q_{0I_2}/V \right)^{-1} \left(p^\circ/kT \right)^{-1} \exp(-D_{I_2}/kT)$$

The molar mass of I is $126.90 \times 10^{-3} \text{kg} \cdot \text{mol}^{-1}$ and that of I_2 is $253.80 \times 10^{-3} \text{kg} \cdot \text{mol}^{-1}$.

$$m_I = [126.90 \times 10^{-3} / (6.022 \times 10^{23})] \text{kg} = 21.07 \times 10^{-26} \text{kg}$$

$$m_{I_2} = [253.80 \times 10^{-3} / (6.022 \times 10^{23})] \text{kg} = 42.14 \times 10^{-26} \text{kg}$$

According to Eqs.(12-113, 12-114),

$$\begin{aligned} q_{0I} kT / (p^\circ V) &= (kT/p^\circ) (2\pi m_I kT/h^2)^{3/2} g_{e,0} \\ &= \frac{13.81 \times 10^{-24} \times 1073}{0.1 \times 10^6} \times \left[\frac{2\pi \times 21.07 \times 10^{-26} \times 13.81 \times 10^{-24} \times 1073}{(0.6626 \times 10^{-33})^2} \right]^{3/2} \times 4 = 5.60 \times 10^9 \end{aligned}$$

$$\begin{aligned} q_{0I_2} kT / p^\circ V &= (kT/p^\circ) (2\pi m_{I_2} kT/h^2)^{3/2} (T/(2\Theta_r)) (1 - e^{-\Theta_r/T})^{-1} q_{0,e} \\ &= \frac{13.81 \times 10^{-24} \times 1073}{0.1 \times 10^6} \times \left[\frac{2\pi \times 42.14 \times 10^{-26} \times 13.81 \times 10^{-24} \times 1073}{(0.6626 \times 10^{-33})^2} \right]^{3/2} \end{aligned}$$

$$\times \frac{1073}{2 \times 0.0537} \times \frac{1}{1 - e^{-309/1073}} \times 1 = 1.58 \times 10^{14}$$

$$K^\circ = (5.60 \times 10^9)^2 (1.58 \times 10^{14})^{-1} \exp\left(-\frac{148.7 \times 10^3}{6.022 \times 10^{23} \times 13.81 \times 10^{-24} \times 1073}\right) = 0.0115$$

Experimental value of K° is 0.0114.

Brief History

The development of the kinetic theory of gases can be considered as the embryo stage of the statistical mechanics. Early in the last half of the 17th century, scientists had understood that the pressure of gases is the result of colliding wall by a large number of molecules. Based on this understanding, in 1738, the Boyle law was derived by a Swiss mathematician Bernoulli D. In 1856, the relation between the gas pressure and the molecular properties such as the

mass, the number density and the moving velocity was derived by Krönig A K of Germany by further using the probability theory. The principle founders of the kinetic theory of gases are a German mathematician and physicist Clausius R J E (also referring to Chapters 2 and 16), a Scottish physicist Maxwell J C (also referring to Chapters 6 and 9) and an Austrian physicist Boltzmann L E. In 1857, Clausius gave an explanation for the Boyle law on the basis of the kinetic theory of gases, and introduced some important concepts for molecules such as the mean square-root velocity, the mean free path and the collision number. In 1860, Maxwell understood that the velocities of different molecules are different and developed the velocity distribution law for molecules. Later, he also established the mathematical theory for transport phenomena in gases. In 1868, Boltzmann introduced the gravitational field into the velocity distribution law and proved this law by using the H theorem. He also gave the statistical meanings for the entropy and completed the mathematical theory for transport phenomena. The methods they used are now called the Maxwell-Boltzmann statistical method primarily for systems without interactions among molecules, for examples, the low pressure gases and the dilute solutions. The method can be used both for the equilibrium properties and for the non-equilibrium rate properties.

The works of Maxwell and Boltzmann were founded on the classical mechanics where the molecular motions are described by the continuous change of coordinates and momentums; therefore, their method is also called the classical statistical method. At the beginning of the 20th century, the quantum mechanics was born. Scientists have gradually understood that the movements of microscopic particles should be described by the wave functions or the quantum states, the changes of them are usually discrete, correspondingly, the quantum statistical method was formed. In 1900, Planck M of Germany (also referring to Chapters 2 and 9) still adopted the Maxwell-Boltzmann statistical method to derive the equation of the black body radiation but supposed that the energy of the harmonic oscillators is discrete. In 1905, Einstein A, a Swiss Germany Scientist (also referring to Chapter 9), proposed the photon theory, it made people think reasonably that the black body radiation could be considered as a photon gas then to derive the radiation equation. This derivation was realized successfully by an Indian physicist Bose S N and was extended later by Einstein. Finally, it was developed to be the Bose-Einstein quantum statistical method. In 1926, Fermi E of Italy (later became an American) found that the Bose-Einstein quantum statistical method could not be used for systems concerning electrons, protons and neutrons, the quantum states of them are restricted by the Pauli exclusion principle. Based on this discovery, Fermi and Dirac P A of the Great Britain (also referring to Chapter 9) developed another method called the Fermi-Dirac quantum statistical method which could describe the behavior of the free electrons in metals and semi-conductors satisfactory. Because of the proof of the new radioactive elements created by the nuclear radiation, and the relevant discovery of the nuclear reactions initiated by slow neutrons, Fermi won the Nobel Prize of physics in 1938. The quantum statistical method has no difference with the classical counterpart in the statistical principle but has difference in the mechanical model adopted. The former uses quantum mechanics while the latter uses classical mechanics. The quantum statistical method is more rigorous and in certain conditions it can reproduce the same results as that by the classical method. The two quantum statistical methods mentioned above also demand

that the particles have no interactions.

For systems with interactions among molecules or particles, the more general statistical mechanics for the dependent-particle systems was developed later, referring to the next Chapter.

Concluding Remarks

The object of the statistical mechanical studying is the macroscopic systems composed of a large number of microscopic particles, the movements of them observe the mechanical principles including classical and quantum. However, because the number of particles is an astronomic number, simply using mechanical principles to obtain the results by solving the equations of motion for all the particles in a system is unrealistic. In practice, some new statistical principles essentially different from the mechanical ones were discovered, ascending to theory, it is the statistical mechanics.

The statistical mechanics has built its own integrate system. The same as that of the thermodynamics and the quantum mechanics, the statistical mechanics is also founded on some fundamental postulates which have been proved correct by practice. There are three postulates (some books adopt two of them, i.e., the second and the third, or one of them, i.e., the third one of this book). The most important one is the postulate of equal a priori probabilities. The statistical mechanics has also its unique methods, the most probable distribution and the maximum term method. Although this chapter only discusses the equilibrium properties of the independent-particle systems, the fundamental postulates and methods elucidated can still be used for the more complex statistical ensemble theory of the dependent-particle systems.

In the thermodynamics, we have known that it is necessary to import some macroscopic characteristic properties of substances to obtain other macroscopic properties by using the general principles connecting various macroscopic properties derived by thermodynamics. The same situation appeared in the statistical mechanics which provides the general principles connecting with the microscopic properties and the macroscopic properties. For the independent-particle systems, the rules are materialized as the general relations between the macroscopic properties and the molecular partition functions. In applications, we should import the microscopic characteristic properties of substances, mainly the translational, the rotational, the vibrational and the electronic energy levels, or the corresponding characteristic parameters such as the molecular mass, the moment of inertia and the vibration frequency. Just as that the thermodynamics can not provide the macroscopic characteristic properties by itself, they should be obtained through the experimental, the semi-empirical or the theoretical method. The latter is the statistical mechanical method. Neither can the statistical mechanics provide the microscopic characteristic properties by themselves. They should also be obtained through the experimental, the semi-empirical or the theoretical method. The latter is the quantum mechanical method. How to obtain the microscopic characteristic properties theoretically is the content of the part III of this book, "The Structure".

However, the statistical mechanics has its limitations. It must use microscopic models. The independent-particle system used in this chapter is a model. The translational particle, the rigid rotator and the simple harmonic oscillator involved are all models. The reason we use models is that our

knowledge of the objective reality is not perfect on the one hand. On the other hand, we have to overcome the difficulties concerning the theories, especially the difficulties of mathematics. Models reflect the essentials of the objective reality, but only approximately. Just due to the approximation, the lack of consistency always appears comparing with the experimental phenomena. It is then demanded to study more accurate models, correspondingly, to study more accurate and effective theories. In the next Chapter, we will study the dependent-particle systems. Because of the consideration of the molecular interactions, the problems of modeling and methods will be more prominent.

General Problems

1. Summarize the differences between the classical and the quantum description for the microscopic state.

2. It is generally stated that the postulate of equal a priori probabilities is the most important postulate, why?

3. Suppose there are three simple harmonic oscillators vibrating on three stationary points O, P and Q, respectively. How many possible distributions does a macroscopic state of the system have when the total energy is $11h\nu/2$? How many microscopic states does each distribution have? Hint: Refer to Eq.(12-4) for the vibrational energy level.

4. For a system composed of a large number of independent particles, can we say that the equilibrium distribution is the most probable distribution?

5. According to the maximum term method, can we say that the thermodynamic probability of a macroscopic state equals that of the most probable distribution?

6. There is a notable difference in form for the distributions in terms of energy levels and in terms of quantum states, why do we still say that they provide the same partition function?

7. What are the merit and demerit of the revision made in the MB distribution for the identical character of the microscopic particles?

8. Why can we say that the molecular partition function is the concentrated materialization of the MB statistical distribution rules?

9. The two expressions for the molecular partition function, Eq.(12-36) and Eq.(12-38), are a summation with respect to the energy levels and to the quantum states. If adopting the latter, what revision shall we take for the derivation of the MB distribution?

10. Whether the molecular partition function is a macroscopic property or a microscopic property?

11. Which of those molecular partition functions is the intensive property, which is the extensive property?

12. The molar isochoric heat capacity of gaseous chlorine Cl_2 at 18°C is $C_{V,m} = 24.7\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ but not $C_{V,m} = 7R/2$, why? Explain the fact by using Θ/T of Cl_2 .

13. Make a review to confirm where we have used the three fundamental postulates of the statistical mechanics.

14. Sum up the effects of the molecular partition function in the statistical mechanics of the independent-particle systems.

15. A substance composed of mono-atomic molecules is in vapor-liquid

equilibrium. The molecules in gas phase can be considered as the independent non-localized particles that the entropy of them can be expressed by the Sackur-Tetrode equation, while the entropy of the liquid phase can be neglected comparing with that of the gas phase. Derive the relation between the vapor pressure and the temperature and compare the result with the Clausius-Clapeyron equation.

16. Two adiabatic containers with equal volume are filled with 1 mol of a gas A at 290K and 1 mol of a gas B, respectively at 300K. They are both composed of mono-atomic molecules. Now open the valve connecting the two containers, A and B are mixed up. Calculate the ratio of the numbers of microscopic states before and mixing them together.

17. In 15.5.6 of Chapter 11, we have mentioned for the mechanism of laser that in between energy levels A and A' shown in Figure 11-12, a population inversion is realized, the number of molecules at the higher energy level is larger than that at the lower energy level. Suppose it is in thermal equilibrium and the MB distribution, Eq.(12-37) is still observed. What logical deduction shall we take for the temperature? (Hint: The system will have a **negative temperature**. It is not a temperature colder than 0K, but hotter than any positive temperature. Refer to: Kittel C, Kroemer H. Thermal Physics. 2nd ed. Appendix E. San Francisco: W H Freeman Company, 1980.)

Numerical Problems

1. A molecule of ideal gas with a mass of m is moving in a cubic box with a size of a . The translational energy is $\varepsilon_t = h^2(n_x^2 + n_y^2 + n_z^2)/8ma^2$, n_x, n_y, n_z , are three translational quantum numbers. What is the degeneracy of a translational energy level with an energy of $14h^2/8ma^2$?

2. 12 balls with different colors are thrown into three boxes where the second has two compartments and the third has three compartments. Suppose a distribution with 7, 4 and 1 balls allocated in the first, second and the third boxes, respectively, what is the number of different forms of allocation for this distribution?

3. Suppose there is a localized-particle system composed of three independent one-dimensional simple harmonic oscillators. If the total energy of the system is $(9/2)h\nu$, ν is the vibration frequency. (1) How many possible distributions in terms of energy levels does the macroscopic state have? (2) How many microscopic states are possessed by each of them? (2) Which distribution has the maximum possibility of appearance?

4. Suppose an independent-particle system is in equilibrium and observes the MB distribution, the lowest five energy levels of the system are: $\varepsilon_0=0$, $\varepsilon_1=1.106 \times 10^{-20}\text{J}$, $\varepsilon_2=2.212 \times 10^{-20}\text{J}$, $\varepsilon_3=3.318 \times 10^{-20}\text{J}$, $\varepsilon_4=4.424 \times 10^{-20}\text{J}$. They are all non-degenerated. The temperature of the system is 300K. Calculate: (1) The Boltzmann factor $e^{-\varepsilon_i/kT}$ of each energy level. (2) The partition function of the particles. (3) The probabilities of finding particles on these five energy levels. (4) The molar energy of the system.

5. Heating N_2 with an arc, the relative numbers of molecules on the vibrational energy levels are determined by spectroscopy shown in the Table. $\Theta_v(\text{N}_2) = 3390\text{ K}$.

v	0	1	2	3	4
N_v/N_0	1.00	0.26	0.07	0.02	0.00

(1) Testify that the allocation of molecules on various vibrational energy levels is in an equilibrium distribution. (2) Calculate the temperature of the gas.

6. Calculate the translational partition functions for the molecules of gases H_2 , CH_4 , C_3H_8 , respectively at 298K in a volume of 1cm^3 .

7. The moment of inertia and the vibration frequency of HI are $42.70 \times 10^{-48} \text{ kg} \cdot \text{m}^2$ and $66.88 \times 10^{12} \text{ s}^{-1}$, respectively. Calculate the rotational partition function q_r and the vibrational partition function q_v and q_{0v} for HI molecules at 100°C .

8. The translational, the rotational and the vibrational partition functions of an ideal gas of diatomic molecules at 300K are: $q_t=10^{30}$, $q_r=10^2$, $q_v=1.1$, respectively. Calculate: (1) The molecular fraction on a translational energy level with $\varepsilon_t=6 \times 10^{-21} \text{ J}$ and $g_t=10^5$. (2) The molecular fraction on a rotational energy level with $\varepsilon_r=4 \times 10^{-21} \text{ J}$ and $g_r=30$. (3) The molecular fraction on a vibrational energy level with $\varepsilon_v=1 \times 10^{-21} \text{ J}$ and $g_v=1$. (4) The molecular fraction when the thermal energy (the sum of the above ε_t , ε_r , ε_v) is $11 \times 10^{-21} \text{ J}$.

9. The vibrational temperature of molecule Cl_2 is $\Theta_v=814 \text{ K}$. Calculate the contribution of the molecular vibrations to the standard molar isochoric heat capacity of Cl_2 at 25°C .

10. N_2O is a linear molecule. Calculate its standard molar isochoric heat capacity at 25°C . The relevant rotational and vibrational temperatures can be obtained in Tables 12-1 and 12-2.

11. In crystals Pb and C (diamond), the vibration frequencies of Pb atom and C atom are $2 \times 10^{12} \text{ s}^{-1}$ and $3 \times 10^{13} \text{ s}^{-1}$, respectively. Calculate their molar isochoric heat capacities at 300K by using the Einstein equation of the crystal heat capacity.

12. Calculate the molar entropy of Ar at the normal boiling point of 87.3 K . The molar mass of Ar is $39.95 \text{ g} \cdot \text{mol}^{-1}$.

13. Calculate the standard molar rotational and vibrational entropies of CO_2 at 25°C . The relevant rotational and vibrational temperatures can be obtained in Tables 12-1 and 12-2.

14. The rotational temperatures of NH_3 are $\Theta_A=14.30 \text{ K}$, $\Theta_B=14.30 \text{ K}$, $\Theta_C=9.08 \text{ K}$. Calculate the molar rotational energy and the standard molar rotational entropy of NH_3 at 298.15 K .

15. The rotational and vibrational temperatures of N_2 molecule are $\Theta_r=2.89 \text{ K}$ and $\Theta_v=3390 \text{ K}$, respectively. The molar mass of N_2 is $28.01 \text{ g} \cdot \text{mol}^{-1}$. Calculate the standard molar entropy of N_2 at 298.15 K .

16. CO is a linear molecule with two orientations in the crystal, CO and OC. Because of the kinetic obstacles, the random arrangement of these two orientations still remains in crystal at 0 K . Calculate the residual entropy of the CO crystal.

17. Calculate the molecular partition function of 1 mol of $\text{H}_2\text{O}(\text{g})$ at 500 K and the standard state by using the data provided in Tables 12-1 and 12-2.

18. Calculate the standard equilibrium constant K° for the gaseous reaction $2\text{HI}=\text{H}_2+\text{I}_2$ at 1000 K by using the data of these diatomic molecules, HI, H_2 and I_2 shown in the following Table.

Molecule	Θ_r/K	Θ_v/K	$D/(\text{kJ} \cdot \text{mol}^{-1})$
HI	9.43	3209	294.97
H_2	87.5	6320	431.96
I_2	0.0537	309	148.74