CHEM-THERMO

A STATISTICAL APPROACH TO CLASSICAL CHEMICAL THERMODYNAMICS

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Preface

Opening a new line of attack on an old pedagogic problem, the statistical analysis developed in this book has not before figured in a truly *elementary* approach to primarily *chemical* thermodynamics. This analysis wholly supplants the Carnot analysis that students find so forbiddingly difficult. And, though superficially more demanding, the statistical analysis has proved readily intelligible to the same kind of students formerly frustrated by Carnot.

The disappearance of Carnot opens the way to a second important simplification. For one can then entirely bypass the great morass of work calculations that has, for generations, claimed its heavy toll of innocent wayfarers on the roads of classical thermodynamics. Apart from the requirements of the Carnot analysis, these stultifyingly traditional calculations are actually of no use whatever to the vast majority of working chemists. And, with the disappearance of all such calculations, the argument can be brought to a sharper focus on just those aspects of thermodynamics that are of greatest relevance to chemistry: most notably, the power to calculate, from purely thermal data, the position of equilibrium in a chemical reaction perhaps not even yet achieved.

Here is the scenario. Chapter 1 opens with a simple but substantive account of Boltzmann statistics, which comes naturally to highlight a parameter W. For readily assignable reasons, we choose to discuss not W itself but, rather, the "entropy" defined by writing $S \equiv k \ln W$. This development wholly dispels the oppressive sense of mystery commonly associated with the concept of entropy. Admittedly, in most cases of actual chemical interest, we find ourselves unable to evaluate W and, thence, S. But we also discover that the definition of S leads at once to a derivative relation applicable to all purely thermal changes. Rendered intuitively meaningful by its definition in terms of W, the concept of entropy is thus shown to be operationally quantifiable by way of purely thermal measurements. And, by a slight extension of the same statistical analysis, we soon arrive at a master-relation that promises *general* criteria for both the direction of spontaneous change and the position of equilibrium ultimately attained in any such change.

Chapter 1 introduces thermodynamics in an informal way. Chapters 2 and 3 then supply a more formal account of the principles of thermodynamics, after which Chapter 4 returns to the full exploitation of the master-relation that is then possible. Focused exclusively on macroscopic parameters, these last three chapters offer a clear view of both the powers and the limitations of a strictly classical thermodynamics. However, those who wish more fully to exploit the statistical viewpoint of Chapter 1 will find it easy to do so: the present text joins smoothly to Part II of my *Elements of Statistical Thermodynamics* (Addison-Wesley, 1968), where a straightforward development of the partition function opens the way to a determination of thermodynamic parameters from spectroscopic data.

In drafting this text I have had in mind the needs of college freshmen whose efforts would be actively supported by a series of exegetical lectures. But I have intended the book also for essentially independent study by more advanced students. Whatever the background of the reader, to follow the argument he will need no more than some familiarity with the leading quantitative concepts of the traditional introductory college chemistry course, together with a sound background in high-school physics and mathematics. Prior acquaintance with the rudiments of the calculus will be very helpful, but Appendix I provides a full development of all of the exceedingly elementary operations of the calculus used in this book. This purely mathematical machinery has everywhere been held to an absolute minimum, in order that it should not (as so often it does) obstruct the student's view of the essential *physical* ideas that lie at the heart of thermodynamics. Despite the modest preparation expected of the reader, this text will prepare him to grapple with the comprehensive set of amply challenging problems presented in Appendix II. Here too the challenge arises from the physical ideas, *not* the mathematical machinery: indeed, most of the problems demand nothing beyond algebra, and the others require no use of calculus beyond the few operations already displayed in the body of the text.

"Work" here becomes so peripheral a topic that, even after thirty years of thinking in terms of the old sign convention, the author has encountered no difficulty whatever in adopting the opposite sign convention now officially recommended. Amongst the myriad equations in the body of the text, some have been denoted by letters or numbers. The letter assignments serve only to facilitate identification of relations operative in the immediately succeeding text, or in a problem. The number assignments, on the other hand, systematically distinguish the most important relations. The reader will be well advised to organize his study by compiling his own list of the 65 numbered equations—attaching to each an indication of any special conditions that restrict its applicability.

Among the many books that have contributed to the shaping of this exposition, undoubtedly the two most influential have been the late Ronald Gurney's *Introduction to Statistical Mechanics* (McGraw-Hill, 1949) and Frederick Reif's *Statistical Physics* (McGraw-Hill, 1965). The treatment of heat-engine efficiencies follows a line suggested in a manuscript by Herbert Callen. A few problems, drawn in substance from other texts, carry the names of the authors to whom I am indebted. Three publishers have kindly permitted me to reproduce certain copyrighted materials, as follows: Tables 2 and 3 have been taken from E. F. Caldin's *Introduction to Chemical Thermodynamics* (Oxford University Press, 1958); Fig. 35 has been redrawn from Hildebrand and Scott's *Solubility of Non-Electrolytes* (Reinhold, 1950); and Fig. 7 comes from J. D. Fast's *Entropy* (Philips Technical Library, Eindhoven, Holland, 1962).

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Cambridge, Massachusetts L. K. N.
December 1971

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The Statistical Viewpoint 1

In every change, however drastic it may appear, we surmise a "something" that remains constant. From the very beginning of the modern era, some men (e.g., Descartes) have conceived that "something" as more or less close kin to what we would call energy. And energy—or, better, mass-energy—*is* surely conceived by us as a "something constant" enduring through all change. The energy concept thus gives quantitative expression to our firm conviction that "plus ça change, plus c'est la même chose." We have another conviction scarcely less intense: the conviction that the future will not repeat the past, that time unrolls unidirectionally, that the world is getting on. This second conviction finds quantitative expression in the concept of entropy (from Gr. *en*, in + *trope*, turning). By always increasing in the direction of spontaneous change, entropy indicates the "turn," or direction, taken by all such change. And from the union of the entropy and energy concepts, little more than a century ago, there was born a notably abstract science with innumerable concrete applications; a science of thermodynamics that combines magnificent generality with unfailing reliability to a degree unrivaled by any other science known to man.

Thermodynamics treats of *systems*—parts of the world that definite boundaries separate conceptually (and often, with a good degree of approximation, physically) from the rest of the world. The condition or *state* of such a system is regarded as thermodynamically defined as soon as values have been established for a small set of measurable parameters. These parameters are so chosen that any particular state of the system will be fully and accurately reproduced whenever the defining parameters take on the set of values descriptive of that state. Temperature, pressure, volume, and expressions of concentration (e.g., mole fractions) are the parameters most used by chemists, and temperature in particular is distinctive of thermodynamic analyses generally. But not every state of every system can be characterized by a single well-defined temperature (and pressure), and from this circumstance arise two major restrictions on the applicability of classical thermodynamics. First, given the (Maxwellian) distribution of molecular velocities, a single molecule, or even a small group of molecules, does not have a definite temperature. Only to *macroscopic* systems will a temperature be assignable, and only to such systems will thermodynamics be applicable. Second, even a macroscopic system will manifest local inhomogeneities of temperature (and pressure) while it is undergoing rapid change. An entire macroscopic system will be characterizable by a unique temperature (and pressure) only when that system stands in an unchanging state of *equilibrium* —or in a quasi-static state only infinitesimally different from a true equilibrium state. And it is with such states alone that classical thermodynamics concerns itself.

Characteristically a science of macroscopic equilibrium systems, thermodynamics will here be developed from an analysis of the submicroscopic components (atoms, molecules, etc.) that constitute all known macroscopic systems. In a bounded system, the crucial characteristic of these components is that their energies are "quantized." That is, where the energies accessible to a macroscopic system form a virtual continuum of possibilities, the energies open to any of its submicroscopic components are limited to a discontinuous set of alternatives associated with integral values of some "quantum number."

Perhaps the most familiar example of what is meant by quantization is presented by the Bohr interpretation of the hydrogen emission spectrum. This spectrum consists of a series of sharp "lines," characterized by particular wavelengths. Each of these lines is supposed to arise in the emission by the hydrogen atom of an energy packet of some particular size. Such an energy packet is emitted when the atom passes from a state of higher energy to one of lower energy. From a study of the sizes of the emitted energy packets, one infers that the atom can exist only in a certain well-defined set of quantum states. The energy (ϵ_H) associated with any of these permissible states is given by the equation:

$$\epsilon_H = -\frac{2\pi^2 me^4}{h^2} \cdot \frac{1}{n^2}.$$

Here h symbolizes Planck's universal constant, m and e respectively represent the mass and charge of the "orbital" electron in the hydrogen atom, and n is a quantum number that can assume any *integral* value within the range 1 to ∞. The possible states of the hydrogen atom, each characterized by some integral value of the quantum number n, are thus linked with the discontinuous set of permissible energies given by the last equation—which expresses the *energy-quantization condition* for the hydrogen atom. Rather more complicated relations, involving additional quantum numbers, express analogous energy-quantization conditions applicable to other species of gaseous atoms.

Like atoms, molecules also can exist only in particular sets of states characterized by different electronic configurations, with which are associated correspondingly restricted series of permissible energy states. But, unlike atoms, molecules exhibit fully quantized modes of energy storage other than that represented by electronic excitation. For example, when in any given electronic state, a molecule may perform various vibrational motions. A study of molecular spectra indicates that, when the vibration can be approximated as a harmonic oscillation, the only permissible values of the vibrational energy (ϵ_v) are given by the equation

$$\epsilon_v = (v + \tfrac{1}{2})h\nu.$$

Here ν is a frequency characteristic of the particular vibration involved, and v is a quantum number that can assume any *integral* value within the range 0 to ∞. The possible vibrational states, each specified by some distinctive integral value of the vibrational quantum number v, are thus linked by the last equation with an evenly spaced set of quantized vibrational energies. The rotational motions of molecules, and the translational motions of both atoms and molecules, are similarly associated with sets of discrete quantum states—to which correspond similarly discontinuous series of permissible rotational and translational energies.

In a full-dress treatment of statistical thermodynamics, a careful analysis of all the different modes of energy storage is indispensable. But, for the modest goal at which we aim, much less will suffice. Concerning the "harmonic oscillator" we need know *nothing* beyond the even energy spacing of its quantum states. And more generally, all we need take as established is that, in atoms and molecules, every mode of energy storage is *quantized.*† We propose then to view a macroscopic thermodynamic system as an assembly of myriad submicroscopic entities in myriad ever-changing quantum states. This may at first seem a completely hopeless pretension. For how can we possibly hope to give any account of an assembly that, if it contains just one mole of material, contains no less than 6×10^{23} distinct units? Even a three-body problem defies solution in a completely analytical form; yet we face a 6×10^{23}-body problem. Actually, just *because* of the enormous numbers involved, this problem proves unexpectedly tractable when we give it a *statistical* formulation. From a consideration of assemblies of quantized

† Though it enormously simplifies the subsequent analysis, this assumption of quantization is not absolutely essential—and is altogether bypassed in a more laborious but purely classical development.

units, in the next section, we develop three propositions that will prove useful in our statistical analysis. Observe that our concern here is *purely mathematical,* and that we could instead obtain the desired propositions by considering, say, in how many different ways a number of balls can be distributed over a set of boxes.

MICROSTATES AND CONFIGURATIONS

For simplicity, let us consider first an assembly of identical units, localized in space, with permissible quantum states that are associated with an evenly spaced set of energies. An assembly meeting these specifications might be an array of identical one-dimensional harmonic oscillators occupying various fixed positions in a schematic crystal lattice. We stipulate *localization* of the oscillators so that, their identity notwithstanding, each will be rendered distinguishable in principle by its unique geometric placement. We stipulate *identity* of the oscillators so that, in the energy-quantization law $\epsilon_v = (v + \frac{1}{2})h\nu$, the characteristic frequency ν will be the same for any among all the oscillators concerned. The quantum states of any such oscillator can then be depicted as shown in Fig. 1. Since all that concerns us is the *spacing* of these levels, for convenience we have chosen to make our reference zero of energy coincident with the energy of the lowest possible quantum state. That is, for this so-called "ground" state with $v = 0$, we now write $\epsilon_0 \equiv 0$. The energy quantum $h\nu$ represents the *constant* margin by which each of the higher ("excited") states surpasses in energy the state immediately below it. To bring any oscillator from its ground state to an excited state characterized by some integral value of v, we need only add v quanta with energy $h\nu$.

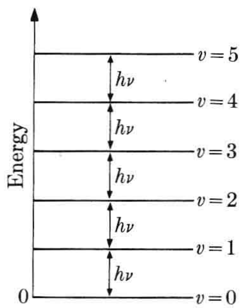

Figure 1

Let us begin with a very simple assembly of three localized oscillators which share three quanta of energy. In how many ways can these three identical quanta be distributed among the three distinguishable oscillators? The ten possible distributions are indicated in Fig. 2—in which the dots are so placed that the letter markings along the abscissa indicate the particular

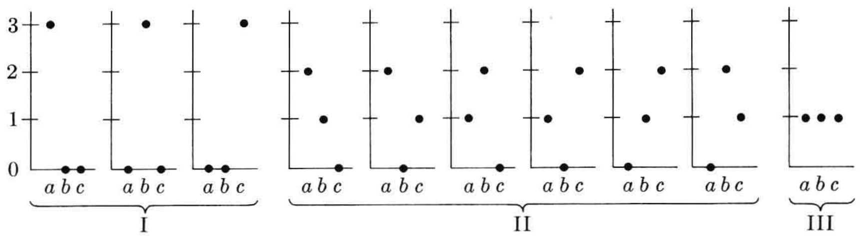

Figure 2

oscillator concerned, and the number of energy quanta assigned to it can be read from the ordinate. Each of the ten detailed distributions we call a *microstate*, and it is easy to see that the ten microstates fall in the three groups indicated by Roman numbers. That is, all ten are simply variants of the three basic *configurations* shown in Fig. 3. In configuration I all three energy quanta are assigned to one oscillator, no quanta to the remaining two oscillators, and three microstates develop from this configuration according to whether the three-quantum packet is assigned to oscillator *a* or to *b* or to *c*. In configuration II two quanta are assigned to some one oscillator, one quantum to a second oscillator, no quanta to the third oscillator; and, as indicated in Fig. 2, there are six distinguishable ways in which such assignments can be made. In configuration III one quantum is assigned to each of the three oscillators, and it is evident that there can be but one microstate associated with this configuration.

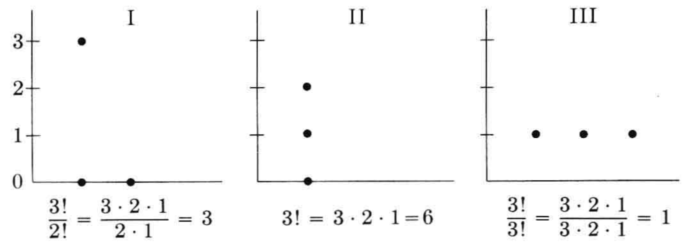

Figure 3

How shall we obtain a systematic count of all the microstates associated with any given configuration? To arrive at the requisite formula, return again to configuration II. Observe that we can assign the first (two-quantum) parcel of energy to any one of three oscillators; having done so, we can assign the second (one-quantum) parcel to either of the two remaining oscillators; there then remains but one oscillator to which we assign the third (nil) parcel. The total number of ways in which the assignments can be made is thus $3 \cdot 2 \cdot 1 = 3!$ (i.e., "three factorial")—which, indeed, duly represents the 6 microstates associated with configuration II. Turning next to configuration I, we have again three choices in assigning the first (three-quantum) parcel, two choices when we assign the second (nil) parcel, and one choice when we assign the third (nil) parcel. But observe that, the last two parcels being the *same*, the final distribution is independent of the *order* in which we assign them. Whether, say, we assign the second parcel to oscillator b and the third parcel to oscillator c, or *vice versa*, the two verbally distinguishable orders result in precisely the *same* final microstate. That is, $2 \cdot 1 = 2!$ verbally distinguishable assignments collapse into 1 microstate because the two oscillators wind up in the *same* ($v = 0$) quantum level. Hence the total number of microstates associated with configuration I is not $3!$ but rather $3!/2! = 3$. The same kind of shrinkage of possibilities is seen in even more extreme form in configuration III. Here there is triple occupancy of the same ($v = 1$) quantum level, and the $3!$ verbally distinguishable assignments collapse into one and the same final microstate. The number of microstates associated with configuration III is then simply $3!/3! = 1$.

By extending this style of analysis, we can easily extract a general formula abundantly useful in more difficult cases. Consider an assembly of some substantial number (N) of localized harmonic oscillators. In how many different ways can we distribute among these oscillators the particular set of energy parcels (including nil parcels) characteristic of the configuration in question? We have N choices of the oscillator to which we assign the first parcel, $(N - 1)$ choices in assigning the second, and so on—representing a total of $(N)(N - 1)(N - 2)\cdots(1) = N!$ distinguishable possibilities if no two of the energy parcels are the same. If, on the other hand, some number (η_a) of the parcels are the same, we can obtain only $N!/\eta_a!$ distinct microstates; if η_a of the parcels are of one kind and η_b of some other one kind, we can obtain only $N!/(\eta_a!)(\eta_b!)$ microstates, and so on. The general conclusion is now quite clear. Symbolizing by W the total number of microstates associated with any configuration involving N distinguishable units, we can write:

$$W = \frac{N!}{(\eta_a!)(\eta_b!)\cdots},$$

where η_a represents the number of units assigned the same number of energy quanta (and, hence, occupying the same quantum level), η_b represents the number of units occupying some other one quantum level, . . .†

† We obtain an identical equation by considering in how many distinct ways a set of balls can be distributed over an equal number (N) of distinguishable boxes. If the balls are all recognizably different from one another, there are $N!$ distinct distributions; but if η_a of the balls are of one kind, and η_b of another, the number of distributions will be reduced to $N!/(\eta_a!)(\eta_b!)$.

The last equation can be represented more compactly as

$$W = \frac{N!}{\prod \eta_n!}, \tag{1}$$

where the symbol $\prod$ instructs us to make a continuing product (even as the symbol $\sum$ instructs us to make a continuing sum) extended over all terms of the form following the symbol, and each of the η_n terms represents the number of units resident in each of the populated quantum levels. Observe that, though we arrived at equation (1) by considering assemblies of harmonic oscillators, with uniform energy spacing between their quantum levels, the actual argument is wholly independent of the supposition of uniformity. *Equation (1) is a general relation*, equally applicable to *any* species of distinguishable unit with *any* energy spacing between its quantum levels. As indicated below, straightforward multiplication of the expanded factorials suffices to establish the number of microstates associated with any configuration for which N is small (<10). For medium-sized values of N (10 to 1000), one can use tabulated values of $N!$ in evaluating W. For very large values of N, we can follow neither of these courses. But, precisely in the limit of large N, an excellent value for $N!$—or, rather, the natural logarithm of $N!$ which we symbolize as $\ln N!$—is supplied by the simplest form of Stirling's approximation,†

$$\ln N! = N \ln N - N. \tag{2}$$

With equation (1) in hand we can make short work of two additional simple examples. Consider that 5 energy quanta are shared among 5 oscillators. The possible configurations, and the number of microstates associated with each of them, are shown in Fig. 4. Note that even a slight increase in the number of units (and quanta) has produced a sharp increase in the total number of microstates $= \sum W_i = 126$.

As a last example, consider an assembly in which the number of energy quanta is *not* equal to the number of units present: suppose that 5 energy quanta are shared among 10 oscillators. The possible configurations of

† Foregoing the elementary application of the calculus that yields a derivation of equation (2), we may just note a crude algebraic argument that offers some rationalization of this form of Stirling's approximation. Consider that the function $N!$ symbolizes the continuing product $(N)(N-1)(N-2)\cdots(2)(1)$. This means a product of N terms with values ranging from a maximum of N to a minimum of 1, and thus averaging about $N/2$. Consequently

$$N! \simeq (N/2)^N$$

$$\ln N! \simeq N \ln (N/2) = N \ln N - N \ln 2 = N \ln N - 0.7 \times N.$$

This proves to be a slight overestimate, which can be much improved merely by replacing the 0.7 by 1.0—and that brings us to equation (2) above.

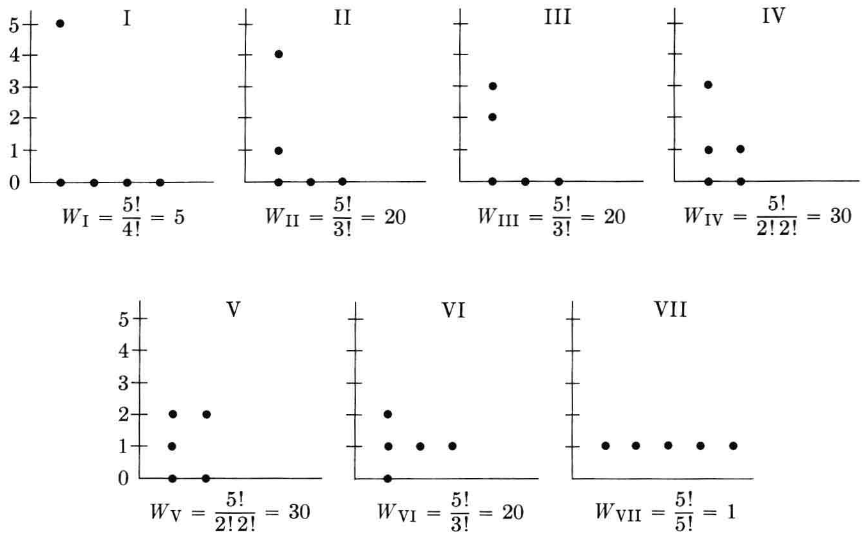

Figure 4

this assembly are easily obtained by adding 5 units to the ground level in each of the configurations shown in Fig. 4—with the results shown in Fig. 5. The calculation of the number of microstates associated with each configuration is given *in extenso*, to call attention to a simple method we will use repeatedly in handling factorial ratios:

$$W_{\mathrm{I}} = \frac{10!}{9!} = \frac{10 \cdot (9!)}{9!} = 10,$$

$$W_{\mathrm{II}} = \frac{10!}{8!} = \frac{10 \cdot 9 \cdot (8!)}{8!} = 10 \cdot 9 = 90,$$

$$W_{\mathrm{III}} = \frac{10!}{8!} = 90,$$

$$W_{\mathrm{IV}} = \frac{10!}{2!7!} = \frac{10 \cdot 9 \cdot 8 \cdot (7!)}{2 \cdot 1 \cdot (7!)} = 10 \cdot 9 \cdot 4 = 360,$$

$$W_{\mathrm{V}} = \frac{10!}{2!7!} = 360,$$

$$W_{\mathrm{VI}} = \frac{10!}{3!6!} = \frac{10 \cdot 9 \cdot 8 \cdot 7 \cdot (6!)}{3 \cdot 2 \cdot 1 \cdot (6!)} = 10 \cdot 12 \cdot 7 = 840,$$

$$W_{\mathrm{VII}} = \frac{10!}{5!5!} = \frac{10 \cdot 9 \cdot 8 \cdot 7 \cdot 6 \cdot (5!)}{5 \cdot 4 \cdot 3 \cdot 2 \cdot 1 \cdot (5!)} = 6 \cdot 7 \cdot 6 = 252.$$

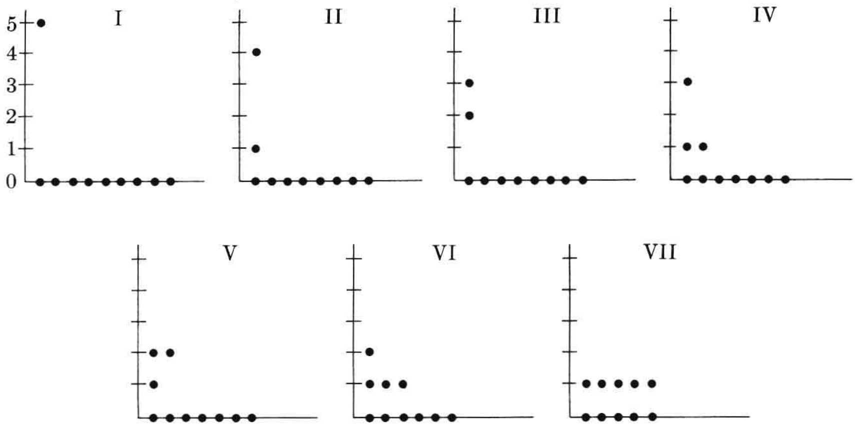

Figure 5

Note that, by doubling the number of units, we have produced close to a ninefold increase in the total number of microstates $= \sum W_i = 2002$.

As the number of units increases further, the total number of microstates skyrockets to unimaginable magnitudes. Thus one can calculate that an assembly of 1000 localized harmonic oscillators sharing 1000 energy quanta possesses more than 10^{600} different microstates. This *is* an unimaginable magnitude: our entire galaxy contains fewer than 10^{70} atoms. Even the estimated total number of atoms in the entire universe is as nothing in comparison with 10^{600}. And though we can offer a compact expression for the total number of microstates that can be assumed by 6×10^{23} oscillators sharing an equal number of energy quanta, that number ($\simeq 10^{10^{23}}$) is essentially meaningless, inconceivably immense.

This explosive expansion of the total number of microstates with increasing N is a direct consequence of the mathematics of permutations, from which arises also a second consequence of no less importance. We can detect the emergence of this further effect in results already obtained. Let us compare our findings for the 5 unit-5 quantum assembly with those for the 10 unit-5 quantum assembly. In Fig. 6 we represent by shaded and open bars respectively the number of microstates associated with each configuration of these two assemblies. If we make the width of each bar equal to one unit of horizontal distance, the numbers of units of area covered by the solid and open bars respectively will indicate the *total* numbers of microstates that can be assumed by the 5-5 and 10-5 assemblies. The ratio of the areas does indeed reflect the approximately 16:1 value earlier established as the ratio of those numbers. But we have yet to note the most significant feature of the graph: the conspicuous peak representing the number of microstates associated with one configuration (VI) of the 10-5 assembly. Where for the