becomes appreciable at small angles and causes excess scattering. The points at small angles, however, cannot be taken as decisive evidence of the latter because at those angles the scattering from the walls of the chamber was larger than at greater angles and the accuracy of the gas readings consequently lower.

In figure 4 it is seen that the oxygen curve is a function of the wave-length. Reduced to the same scale as the hydrogen curve at 70° it shows that excess scattering for θ less than about 60° is very prominent. A few observations with carbon dioxide gave a curve hardly distinguishable from that for oxygen; excess scattering appeared at approximately the same angle. Work on other gases is in progress.

One may conclude on the basis of these experiments that interference is present in X-rays scattered from a single molecule of carbon dioxide or oxygen, and absent in rays scattered from a hydrogen molecule—at least in the range 30° to 90°. This may be interpreted as evidence of considerably unmodified radiation in the former case and of completely or nearly completely modified radiation in the latter, confirming Woo's measurements and in accord with Jauncey's theory of the intensities of the different kinds of radiation in the Compton effect.

It is a pleasure to acknowledge the many helpful suggestions of Prof. A. H. Compton, Prof. P. A. Ross and Dr. J. A. Bearden.

[1] Compton's *X-Rays and Electrons*, p. 74, gives complete references and a summary of the work in this field.

[2] Debye, P., *Phys. Zeit.*, **28**, 135, 1927.

[3] Mark and Schocken, *Naturwiss.*, **15**, 139, 1927 (Feb. 11).

THE DISTRIBUTION OF ENERGY IN MOLECULES

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The author has recently attempted to account for the rates of unimolecular reactions by a theory[1] which assumes activation by collision and treats the reacting molecules as mechanical systems with many internal degrees of freedom. A somewhat similar theory had been advanced earlier by Rice and Ramsperger.[2]

For the complete development of the author's theory it is necessary to solve the problem: Given a number of oscillators, classical or quantum, harmonic or otherwise, and a value for the total energy of these oscillators, calculate the chance that a specified one of the oscillators shall have energy in excess of some given value. The solution of this problem for the case

of classical harmonic oscillators was given in the author's first paper. The methods used there, however, were somewhat elementary and not suitable for more complex cases.

The problem may be solved, in general, by a consideration of the total phase-space volumes associated with various conditions of the molecule. Some of the special cases have been worked out, and will be considered here.

Case I—Classical Oscillators.—Suppose that there are s classical oscillators, and that the energy of the ith oscillator is given by

$$\epsilon_i = p_i^2 + q_i^2.$$

The coördinates may always be transformed so that this form is obtained, rather than

$$\epsilon_i = \tfrac{1}{2}b_i p_i'^2 + \tfrac{1}{2}a_i q_i'^2.$$

Then, from the well-known formula[3] for the volume of an n-dimensional sphere, the phase-space volume corresponding to molecules with energy between ϵ and $\epsilon + d\epsilon$ is

$$\int \cdots \int_{\sum_1^s (p_i^2 + q_i^2) = \epsilon}^{\epsilon + d\epsilon} dp_1 \ldots dp_s dq_1 \ldots dq_s = \frac{\pi^s}{\Gamma(s+1)} \left[(\epsilon + d\epsilon)^s - \epsilon^s \right]$$

$$= \frac{\pi^s}{\Gamma(s)} \epsilon^{s-1} d\epsilon.$$

The volume corresponding to states in which the total energy lies within the limits ϵ and $\epsilon + d\epsilon$ and in which a specified oscillator has energy at least ϵ_0 is[4]

$$\int_{p_1^2 + q_1^2 = \epsilon_0}^{\epsilon} \int dp_1 dq_1 \int \cdots \int_{\sum_2^s (p_i^2 + q_i^2) = \epsilon - p_1^2 - q_1^2}^{\epsilon - p_1^2 - q_1^2 + d\epsilon} dp_2 \ldots dp_s \, dq_2 \ldots dq_s$$

$$= \int_{p_1^2 + q_1^2 = \epsilon_0}^{\epsilon} \int \frac{\pi^{s-1}}{\Gamma(s-1)} \left(\epsilon - p_1^2 - q_1^2 \right)^{s-2} d\epsilon dp_1 dq_1.$$

This may be conveniently integrated by the substitutions

$$p_1 = \sqrt{z} \cos \theta,$$

$$q_1 = \sqrt{z} \sin \theta,$$

where, by Jacobi's theorem, we must substitute

$$dp_1 dq_1 = \tfrac{1}{2} dz d\theta.$$

The result is

$$4 \int_{\epsilon_0}^{\epsilon} \int_0^{\pi/2} \frac{\pi^{s-1}}{\Gamma(s-1)} (\epsilon - \epsilon_0)^{s-2} \cdot \tfrac{1}{2} d\epsilon d\theta d\epsilon_0$$

$$= \frac{\pi^s}{\Gamma(s)} (\epsilon - \epsilon_0)^{s-1} d\epsilon.$$

The ratio of this volume to the total volume associated with energy ϵ to $\epsilon + d\epsilon$, namely

$$\left(\frac{\epsilon - \epsilon_0}{\epsilon} \right)^{s-1},$$

is the chance that when the s oscillators have energy between ϵ and $\epsilon + d\epsilon$ a specified one will have energy greater than ϵ_0.

Case II—Quantum Oscillators of a Single Frequency.—Suppose that there are s quantum oscillators all of the frequency ν. Let the group have n quanta; calculate the chance that some one of the oscillators has at least m quanta.

We shall assume that the μ weight for each microscopic state of the system is h^s, and that there is no difficulty due to a greater μ weight for the lowest state. Then the total μ weight associated with the system when it contains n quanta is

$$h^s \cdot \frac{(n + s - 1)!}{n!(s - 1)!} = h^s \binom{n + s - 1}{n}$$

since the number of distinct arrangements of n objects into s groups is

$$\binom{n + s - 1}{n}.$$

The μ weight of those states in which a chosen oscillator has at least m quanta is[5]

$$\sum_{m=m}^{n} h \cdot h^{s-1} \binom{n - m + s - 2}{n - m}.$$

Upon writing $n - m = p$, this becomes

$$h^s \sum_{p=0}^{p} \binom{p + s - 2}{p},$$

and it is well known that the value of this sum is[6]

$$h^s \binom{p + s - 1}{p}.$$

Hence, the μ weight of those states in which the chosen oscillator has at least m quanta is

$$h^s \binom{n - m + s - 1}{n - m}$$

and the ratio of this to the total μ weight gives the chance that when the s oscillators have n quanta, a chosen one will have at least m quanta. This is

$$\frac{n!(n - m + s - 1)!}{(n - m)!(n + s - 1)!}.$$

It is very easy to show that when both n and $n - m$ are very large this reduces to the classical form,

$$\left(\frac{\epsilon - \epsilon_0}{\epsilon}\right)^{s-1},$$

as of course it must.

Case III—Classical Oscillators and Quantum Oscillators of a Single Frequency.—(A.) Accumulation of energy in a quantum oscillator. Suppose that there are s classical oscillators, and r quantum oscillators, all of frequency ν. Then the total μ weight corresponding to energy between ϵ and $\epsilon + d\epsilon$ is[7]

$$\sum_{q=0}^{n} h^r \binom{q + r - 1}{q} \int \overset{\epsilon - qh\nu + d\epsilon}{\underset{\frac{s}{2}(p_i{}^2 + q_i{}^2)\, \epsilon\, -\, qh\nu}{\dots}} \int dq_1 \dots dq_s\, dp_1 \dots dp_s$$

$$= \frac{\pi^s}{\Gamma(s)} h^r d\epsilon \sum_{q=0}^{n} \binom{q + r - 1}{q} (\epsilon - qh\nu)^{s-1}.$$

Here n is the greatest number of quanta which an oscillator can have; it is defined by the inequality

$$n \leqq \frac{\epsilon}{h\nu} < n + 1.$$

Now the μ weight of the states in which the total energy is between ϵ and $\epsilon + d\epsilon$ and in which a chosen quantum oscillator has at least m quanta is[8]

$$\sum_{p=m}^{n} h \cdot \frac{\pi^s}{\Gamma(s)} h^{r-1} d\epsilon \sum_{q=p}^{n} \binom{q - p + r - 2}{q - p} (\epsilon - qh\nu)^{s-1}.$$

Note that

$$\sum_{p=m}^{n} \sum_{q=p}^{n} f(q, p) = \sum_{q=m}^{n} \sum_{p=m}^{q} f(q, p).$$

This may be seen by writing out the sum in a square array. Using this result, we get

$$\frac{\pi^s}{\Gamma(s)} \, h^r d\epsilon \sum_{q=m}^{n} (\epsilon - qh\nu)^{s-1} \sum_{p=m}^{q} \binom{q-p+r-2}{q-p}$$

$$= \frac{\pi^s}{\Gamma(s)} \, h^r d\epsilon \sum_{q=m}^{n} \binom{q-m+r-1}{q-m} (\epsilon - qh\nu)^{s-1}.$$

The ratio of this to the total μ weight gives the chance that the quantum oscillator will have at least m quanta. This is

$$\frac{\displaystyle\sum_{q=m}^{n} \binom{q-m+r-1}{q-m} (\epsilon - qh\nu)^{s-1}}{\displaystyle\sum_{q=0}^{n} \binom{q+r-1}{q} (\epsilon - qh\nu)^{s-1}}.$$

(*B.*) Accumulation of energy in a classical oscillator. Let there be s classical oscillators, and r quantum oscillators of frequency ν, just as before. The total μ weight of the states in which the energy of the system is between ϵ and $\epsilon + d\epsilon$ is the same as before. The μ weight of those states in which a chosen classical oscillator has energy at least ϵ_0 is[9]

$$\frac{\pi^s}{\Gamma(s)} \, h^r d\epsilon \sum_{p=0}^{n-m} \binom{p+r-1}{p} (\epsilon - ph\nu)^{s-1}$$

where n and m are defined by the inequalities

$$n \leqq \frac{\epsilon}{h\nu} < n + 1,$$

$$n - m \leqq \frac{\epsilon - \epsilon_0}{h\nu} < n - m + 1.$$

The ratio gives the chance we want, namely

$$\frac{\displaystyle\sum_{p=0}^{n-m} \binom{p+r-1}{p} (\epsilon - ph\nu - \epsilon_0)^{s-1}}{\displaystyle\sum_{p=0}^{n} \binom{p+r-1}{p} (\epsilon - ph\nu)^{s-1}}.$$

This may be put in the alternative form

$$\frac{\displaystyle\sum_{q=m}^{n} \binom{q-m+r-1}{q-m} (\epsilon - qh\nu + mh\nu - \epsilon_0)^{s-1}}{\displaystyle\sum_{q=0}^{n} \binom{q+r-1}{q} (\epsilon - qh\nu)^{s-1}},$$

which is very similar to that for accumulation of energy in a quantum oscillator since, in general, $mh\nu$ is about equal to ϵ_0. For the classical case it is not possible to define m by a single equation, but the notation preserves the formal identity between the two cases as much as possible. Indeed, when ϵ_0 is an integral number of quanta, then $mh\nu = \epsilon_0$, and the two chances become identical. This gives us the very important result:

In a group of oscillators, some of which are classical and some quantum, all the quantum oscillators having the same frequency, the chance that a given classical oscillator shall have energy equal to or greater than that of m quanta, is exactly the same as the chance that a given quantum oscillator shall have m or more quanta. It is, of course, necessary that the entire group be in statistical equilibrium.

Thus, when the quantum frequencies are not too high, or the temperature of the system too low, the distribution of energy among the oscillators is not markedly different for the quantum oscillators from that for the classical. It will, however, usually be very much different from that which would exist if all the oscillators were classical or all quantum. This difference will be most marked when we consider the chance that an oscillator shall have a large share of the total energy.

This is illustrated by the following short table, constructed for five classical oscillators and five quantum oscillators, with a total energy equivalent to 20 quanta. The second column gives the chance that an oscillator of this group shall have energy equivalent to at least the number of quanta given in the first column. The third column gives the corresponding chance if all the oscillators were classical, and the fourth if they were all quantum.

TABLE 1

m	MIXED CHANCE	PURE CLASSICAL CHANCE	PURE QUANTUM CHANCE
0	1.000	1.000	1.000
5	0.102	0.751×10^{-1}	0.131
10	0.471×10^{-2}	0.195×10^{-2}	0.922×10^{-2}
15	0.395×10^{-4}	0.381×10^{-5}	0.200×10^{-3}
19	0.105×10^{-7}	0.195×10^{-11}	0.998×10^{-6}
20	0	0	0.998×10^{-7}

Thus it appears that the tendency for energy to accumulate in a single oscillator, other conditions being equal, is much greater for quantum oscillators than for classical, when all the oscillators are of one kind; when they are of both kinds, the chance becomes much more nearly the same for the two kinds, and lies between the two pure chances.

Case IV—Classical Oscillators and Quantum Oscillators of Two Frequencies.—It is not hard to extend the preceding results to the case of quantum oscillators of two frequencies and classical oscillators, although

the formulas become more complex. The result for accumulation of energy in a classical oscillator will be given here. The others are very similar.

Suppose that there are s classical oscillators, r quantum oscillators of frequency ν, and t quantum oscillators of frequency μ. Let the entire system have energy between ϵ and $\epsilon + d\epsilon$. Then the chance that a single selected classical oscillator will have energy at least e_0 is found to be

$$\frac{\sum_{p=0}^{k} \sum_{q=0}^{l(p)} \binom{p+r-1}{p} \binom{q+t-1}{q} (\epsilon - ph\nu - qh\mu - \epsilon_0)^{s-1}}{\sum_{p=0}^{n} \sum_{q=0}^{l'(p)} \binom{p+r-1}{p} \binom{q+t-1}{q} (\epsilon - ph\nu - qh\mu)^{s-1}}$$

where

$$n \leqq \frac{\epsilon}{h\nu} < n + 1,$$

$$k \leqq \frac{\epsilon - \epsilon_0}{h\nu} < k + 1,$$

$$l(p) \leqq \frac{\epsilon - \epsilon_0 - ph\nu}{h\mu} < l(p) + 1,$$

$$l'(p) \leqq \frac{\epsilon - ph\nu}{h\mu} < l'(p) + 1.$$

It is fairly evident how to extend this formula to still more complex cases, merely by analogy, though the specification of the upper range of summation becomes increasingly complicated.

The application of these results to the theory of unimolecular reactions will be considered in another place, but it may be said here that, while it would be possible to account for the decomposition of nitrogen pentoxide, using 15 classical internal degrees of freedom (this is nearly the maximum possible for a mechanical system of seven mass-points), when these degrees of freedom are quantized, with frequencies so selected as to give reasonable specific heat values, it is no longer possible to account for the observed rates by the author's theory. Furthermore, it is evident from the results which have been given that no combination of classical and quantum oscillators could be much more effective in accounting for these rates than any other combination of the same number of oscillators with the same internal energy at the temperatures of interest.

These results are all for harmonic oscillators. It will be shown in a subsequent article, however, that there is no help to be obtained by the introduction of a special type of anharmonic oscillator, which has a certain formal resemblance to a chemical bond.

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[1] Kassel, L., article to appear soon in *J. Phys. Chem.*

[2] Rice, O. K., and Ramsperger, H. C., *J. Amer. Chem. Soc.*, **49**, 1617 (1927).

[3] See, for example, Tolman, *Statistical Mechanics with Application to Physics and Chemistry*, Chemical Cat. Co., New York, **1927**, p. 129.

[4] This evidently gives only that part of the preceding volume for which $p_1^2 + q_1^2$ is at least equal to ϵ_0. The same sort of integration will be made repeatedly in this paper.

[5] The μ weight for any state of a single oscillator is h; we extend the summation from $m = m$ to $m = n$, since we want all states in which the single oscillator has at least m quanta.

[6] See, for example, Laska, W., *Sammlung von Formeln der reinen und angewandten Mathematik*, Vieweg und Sohn, Braunschweig, p. 15. But the proof is very easily given by induction.

[7] The integral gives the contribution to the product of the classical oscillators; this is multiplied by the quantum contribution, and the sum taken over all possible total energies for the quantum oscillators.

[8] The expression following the first h is the total μ weight for s classical oscillators and $r - 1$ quantum oscillators, with total energy between $\epsilon - qh\nu$ and $\epsilon - qh\nu + d\epsilon$.

[9] To get this, we multiply the contribution of r quantum oscillators with p quanta by that of s classical oscillators with energy between $\epsilon - ph\nu$ and $\epsilon - ph\nu + d\epsilon$ and at least ϵ_0 in a single oscillator, and sum over all possible values of p.

THE LIFE OF ATOMIC STATES AND THE INTENSITY OF SPECTRAL LINES

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It has recently been possible to explain most of the strong nebular lines as lines arising from electron jumps from metastable states in oxygen and nitrogen.[1] In the nebulae the emission of spectral lines can be observed under conditions of much higher rarefaction than can be found in any other terrestrial or astronomical source. Since these nebular lines occur only under these conditions, this very definitely indicates that the electron jumps causing them take place spontaneously without the interference of outside fields due to other ions, that can often be used to explain jumps of this sort when they are observed in terrestrial sources. *This constitutes then the first direct evidence that metastable states are not absolutely metastable but are states of long mean life, i.e., states from which the probability of a spontaneous jump in unit time is very small.*

Further evidence for this viewpoint is found in the observation by Rayleigh[2] that the forbidden mercury line ^1S-$^3P_2$ at 2270 Å is absorbed about 1/1,000,000 as strongly as the ^1S-$^3P_1$ line at 2536 Å. Since there