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Elementary derivation of the Saha equation

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(Received 1 September 1978; accepted 6 November 1979)

The condition of equilibrium molecular dissociation is investigated without using thermodynamic reasoning explicitly. The approach of "phase-space maximization" illuminates the basic principles of statistical mechanics while providing an understanding of an equation which is useful in many applications.

INTRODUCTION

My statistical mechanics professor had just described an experiment in which molecular hydrogen gas is heated to about 4000 K, and noted that already, at this temperature, some of the molecules are dissociated. "Why should this be," he asked, "when the energy of dissociation corresponds to a temperature of about 50 000 K?" Not realizing that the question was rhetorical, I eagerly raised my hand and volunteered the following explanation: a very small (but nonzero) fraction of the colliding pairs of molecules have sufficient energy to dissociate a molecule; when they do break up a molecule, it is exceedingly difficult for the atoms to recombine since a three-body interaction is required if energy and momentum are to be conserved. He thanked me profusely, adding "that is *precisely* the wrong answer I wanted!" He then explained to the class that my description centered on the kinetic details of the interaction, and was far less general than the statistical mechanical point we were exploring; dissociation creates a larger total number of particles, and thus greatly increases the total volume in phase space.

That is not the sort of classroom encounter one readily forgets, and so a dozen years later I returned to his line of reasoning when I had to derive the equation of dissociation equilibrium for a class of my own. This equation, generally referred to as the Saha equation, is usually found by maximizing the free energy, or by employing some other thermodynamic approach. The approach of "phase-space maximization," however, points directly to the Saha equation without requiring a thorough understanding of thermodynamics. One does not even have to take a derivative to determine the maximum volume in phase space!

Let us consider, then, a gas at temperature T in a fixed volume V, containing M diatomic molecules and A atoms. Since we will assume that the total number of nuclei is fixed, we have

$$2M + A = 2M^\circ, \qquad (1)$$

where M° represents the number of molecules present when the temperature is so low that none are dissociated. The volume in phase space, which we propose to maximize, consists of the sum (over all possible states of the system) of the probability that each state is occupied.

NUMBER OF INTERNAL STATES Γ_I

Let us start with the easy part: how many possible molecular states are there? The relative probability that a state with energy E is occupied at temperature T is given by the Boltzmann factor

$$P(E) = \text{const} \times e^{-E/kT}. \qquad (2)$$

This relationship (often hazily remembered by students as being related somehow to factorials, Stirling's approximation, and Lagrange multipliers) is actually very general. It is the only functional form that meets some basic requirements:

(i) The probability of realizing a configuration of a system which is itself the combination of two subsystems is the *product* of the probabilities of the subsystems combined (independent probabilities multiply).

(ii) The energy of a system which is the combination of two subsystems is the *sum* of the energies of the subsystems combined (changes in "surface energy" can be ignored).

(iii) Higher energy states are less probable (hence, the minus sign).

The factor k (Boltzmann' constant) just expresses the relationship between the units of energy and temperature. The appearance of the temperature in this specific manner was found by requiring agreement with the thermodynamic concept of temperature.

Suppose that the molecules have quantized energy levels with energy E_i which are related to vibration and rotation. Some of these levels may have the same energy, i.e., may be *degenerate*. For each energy level E_i, we denote the number of states having this energy by the factor g_i. The listing of E_i and g_i is the only information concerning the molecule that we need to know. It is usually found experimentally by unraveling the infrared spectrum of the molecule, but can often be determined theoretically with sufficient accuracy.[1] For each molecule, the average number of occupied internal states is

Γ_I = sum over states of {the number of states having energy E_i} times {the probability that state i is occupied}

or

$$\Gamma_I = \sum_i g_i e^{-E_i/kT}. \qquad (3)$$

There is some energy E_{diss} at which the discrete states blend together into a continuum. Because there is a finite width of the discrete levels (which generally increases with increasing pressure), this dividing line is a little difficult to define precisely. Without obscuring the problem, we will simply refer to this energy as the dissociation energy E_{diss}. It is convenient to redefine the bound molecular states with reference to E_{diss}:

$$E_i = W_i - E_{\text{diss}}. \qquad (4)$$

The average number of occupied internal states of each molecule can then be written as

$$\Gamma_I^M = e^{+E_{\text{diss}}/kT} \sum g_i e^{-W_i/kT}. \tag{5}$$

The sum is over all states whose energy W_i is less than E_{diss}.

Assume that atoms have a fixed number of possible internal states, i.e., $\Gamma_I^A = G$. If each atom has a total angular momentum $j\hbar$, this factor is just $j(j + 1)$.

NUMBER OF CONTINUUM STATES

There is also a dense collection of quantum levels associated with the translational motion of the center of mass of each atom or molecule. How can we relate an essentially continuous range of possible translational energies to a number of discrete quantum states? The key is to note that one quantized state occupies a volume of (Planck's constant)^n in the phase space related to motion in n dimensions. The volume in phase space due to continuum motion can be calculated and divided by h^n (not $\hbar^n!$) to determine the equivalent number of discrete states.[2] Following this simple prescription gives the number of states attributable to the continuous spectrum.

$$\Gamma_c = \frac{1}{h^3} \int dv \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y$$
$$\times \int_{-\infty}^{\infty} dp_z \exp(-p_x^2 + p_y^2 + p_z^2/2mkT). \tag{6}$$

We have used the same Boltzmann factor to weight those continuum states and have used the kinetic energy for the total energy. The neglect of interatomic potential energy terms is an approximation (an "ideal gas" of atoms and molecules).

The mass m is either the mass of an atom or a molecule, depending on which we are considering at the moment. We will assume for simplicity that our molecules are homonuclear diatomic, so that the molecular mass is just twice the atomic mass m, and all atoms have the same mass. Each momentum integral gives a factor $\sqrt{2\pi mkT}$ so the average number of atomic translational states is

$$\Gamma_C^A = (2\pi mkT/h^2)^{3/2} V, \tag{7}$$

and the average number of molecular translational states is

$$\Gamma_C^M = (4\pi mkT/h^2)^{3/2} V. \tag{8}$$

PUTTING IT ALL TOGETHER

The total number of possible quantum states for any macroscopic system is inconceivably huge, but we will compute it anyway! Assuming the individual atoms and molecules are independent (that is, the number of possible states of each does not depend on the presence of the others), the total number of states Γ is the product

$$\Gamma = (G\Gamma_C^A)^A (\Gamma_I^M \Gamma_C^M)^M. \tag{9}$$

Actually, this is not quite right, and the necessary correction has deep significance. Since the individual atoms and molecules are indistinguishable, we do not care which atom of molecule is in a particular state. To obtain the correct Γ, divide by $A!M!$, the number of irrelevant reorganizations of the individual atoms and molecules,

$$\Gamma = \frac{1}{A!} (G\Gamma_C^A)^A \frac{1}{M!} (\Gamma_I^M \Gamma_C^M)^M. \tag{10}$$

The values for A and M which maximize this incredible number, subject to the constraint (1), describe the dissociation equilibrium.[3]

To derive a general expression for the equilibrium, let us imagine that we dissociate just one molecule. Then

$$M \rightarrow M - 1,$$
$$A \rightarrow A + 2. \tag{11}$$

If we are really at a maximum of Γ, this small change should not alter Γ at all. When the expressions for before and after the single dissociation are equated, we obtain

$$\frac{1}{A!} (G\Gamma_C^A)^A \frac{1}{M!} (\Gamma_I^M \Gamma_C^M)^M$$
$$= \frac{1}{(A+2)!} (G\Gamma_C^A)^{A+2} \frac{1}{(M-1)!} (\Gamma_I^M \Gamma_C^M)^{M-1} \tag{12}$$

or

$$(A + 2)(A + 1)/M = (G\Gamma_C^A)^2 / \Gamma_I^M \Gamma_C^M. \tag{13}$$

For any macroscopic system, $A \gg 1$, so the equation becomes

$$\frac{A^2}{M} = \frac{G^2 (2\pi mkT/h^2)^{3/2} V}{2^{3/2} \sum_i g_i e^{-W_i/kT}} \exp(-E_{\text{diss}}/kT). \tag{14}$$

This equation, which is the Saha equation of dissociation equilibrium, together with Eq. (1), determines the equilibrium numbers of A and M for a given temperature. It can be rewritten in terms of n_A and n_M, the number of atoms and molecules, respectively, per unit volume, as

$$\frac{n_A^2}{n_M} = \frac{G^2}{2^{3/2} Z} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \exp(-E_{\text{diss}}/kT), \tag{15}$$

where

$$Z = \sum_i g_i e^{-W_i/kT} \tag{16}$$

is known as the partition function.

CONCLUSION

The most important factors in this equation are the exponential and the term to the $3/2$ power. For hydrogen molecules, $E_{\text{diss}}/K \approx 50\,000$ K, and the atom has mass $m = 1.6 \times 10^{-27}$ kg. At $T = 4000$ K, as cited in our introduction, the partition function of the hydrogen molecule is about 35.[4]

Equation (15) then gives

$$\frac{n_A^2}{n_M} = \frac{1}{2^{3/2} \times 35} (4.5 \times 10^{31})(3.7 \times 10^{-6})$$
$$\approx 1.7 \times 10^{24}. \tag{17}$$

The total number of particles can be determined by using the ideal gas law. For a pressure of one atmosphere, very nearly 10^5 N/m^2, this gives

$$n_M + n_A \approx 2 \times 10^{24}. \tag{18}$$

Equations (17) and (18) can be solved simultaneously, yielding

$$n_M = 0.8 \times 10^{24},$$
$$n_A = 1.2 \times 10^{24}. \tag{19}$$

We can now use Eq. (1) to determine that the initial number

density of molecules was 1.4×10^{24}, at room temperature, before any dissociation occurred, the pressure was thus only about 0.06 atm.

Reviewing the numbers in Eq. (17), we see that the very low Boltzmann probability of 3.7×10^{-6} was offset by the (3/2)-power term of 4.5×10^{31}. This latter term, representing the volume in phase space for the atoms, is the real reason that dissociation occurs even when KT is only a tiny fraction of the energy required to break up a molecule.

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[1] Molecules can also have quantized energy levels due to excitation of their electrons. As a practical matter, however, any temperature which is high enough to excite electrons will cause dissociation of any known molecule. Equations very similar to the one we are after, but describing the equilibrium amounts to various ionization levels of atoms, could be derived by considering the states of electronic excitation.

[2] The area of p-x space enclosed by the "orbit" of the one-dimensional harmonic oscillator

$$p^2/2m + kx^2/2 = E$$

is

$$2\pi E \sqrt{m/k}.$$

If $E = \hbar\sqrt{k/m}(n + \frac{1}{2})$, each state of this quantized oscillator occupies a volume $2\pi\hbar$. See, for example, Robert Eisberg and Robert Resnick, *Quantum Physics* (Wiley, New York, 1974), pp. 121–123.

[3] The logarithm of this quantity Γ is the entropy, and we see that maximizing Γ means maximizing the entropy. It is not an accident that entropy is the logarithm of Γ. We want to define a quantity which is proportional to the size of the system, and Γ is the product of independent factors. The logarithm of Γ is thus proportional to the number of atoms and molecules present.

[4] Without going into too much detail, we note that the molecular vibration states have energy $E_n = (n + 1/2)\Delta E$, where ΔE is about 8.7×10^{-20} J. Each of these states has a degeneracy of 1. The rotation states have energy $E_J = \hbar^2 J(J + 1)/2I$, where $I = \mu r^2$, the moment of inertia, is about 4.4×10^{-48} kg m^2. Each of these states has a degeneracy of $(2J + 1)$. Using Eq. (16), one calculates separate partition functions for vibration and rotation and then multiplies them. This assumes that the vibrational and rotational motions are independent, which is not strictly correct. Also, the rotational partition function is one-half of what Eq. (16) gives because of the identity of the two atoms making up this molecule. Data and discussion on vibration–rotation spectra can be found in Eisberg and Resnick (see Ref. 2, pp. 459–467).

ANNOUNCEMENT

The European Physical Society

The European Physical Society, which has made its mark on the multifarious scientific publications of Europe by awarding the "Europhysics Journal" cachet to journals of high quality, has now, in collaboration with the Institute of Physics of the United Kingdom, sponsored a regular scientific publication of its own, the *European Journal of Physics*, with an Editorial Board drawn from member countries of the EPS. The Eur. J. Phys. will, to some extent, resemble the Am. J. Phys. It has come into being as a recognition of the need, in Europe, for a journal devoted to the exchange of ideas on physics as it is taught in universities and other institutes of higher education, and which will provide a forum for the discussion of new, and possibly controversial ideas on well-established topics in physics.

The journal will be published from the Institute of Physics Publishing Division, Techno House, Redcliffe Way, Bristol BS1 6NX, England. The first issue is promised for June, 1980. The editor is Professor G. W. Series of the University of Reading, U.K.