is equal to the matrix invariant,[3] Spur $e^{-H/kT}$. Now the Hamiltonian matrix H has the structure

$$H = H_0 + p_x E_x + p_y E_y + p_z E_z,$$

where p_x, p_y, p_z are the components of the electric moment matrices of the structural unit (atom, molecule or microcrystal) along the three coordinate axes. In the final system of representation which diagonalizes the total energy H, the W_a's may be complicated functions of E_x, E_y, E_z but in the initial system, which is ordinarily used before application of the field, and which diagonalizes only H_0, the elements of H_0, p_x, p_y, p_z are all independent of E, so that the expansion of Z will take the form (2) when the matrices $e^{-H/kT}$ are developed in a Taylor's series in E. Because of the invariance of the diagonal sum, the form (2) is, of course, also preserved in the final system. To prove Eqs. (1), we have only to note that the components of the polarization are given by formulas such as[4]

$$P_x = NkT\partial \log Z/\partial E_x. \tag{3}$$

The coefficients α_i in (2) vanish if there is no residual polarization, as we have tacitly assumed. Since $D_x = E_x + 4\pi P_x$ we thus see that for small fields, Eqs. (1) are valid with $\epsilon_{ij} = \delta_{ij} + 8\pi\beta_{ij}$. An analogous proof can, of course, also be constructed in classical theory. Classically, the partition function Z is an integral over phase space rather than the diagonal sum of a matrix, but still depends on E in the simple fashion (2).

Two incidental remarks about (1) are the following. (a) The coefficients ϵ_{ij} in (1) are functions of temperature due to changes in population of the different stationary states, as well as to changes in the constants of the crystalline structure. As O. M. Jordahl shows elsewhere in the present issue, the principal magnetic axes consequently may vary with temperature. (b) If a crystal has hexagonal

symmetry two of the constants must be equal after the cross terms $\epsilon_{ij}(j \neq i)$ have been made to vanish by transformation to the principal magnetic axes. It is thus impossible to have different initial susceptibilities or Faraday rotations in different directions perpendicular to the "optic" axis in hexagonal crystals. This statement applies quite generally, even with Heisenberg exchange effects, interatomic valence forces, etc., provided only that saturation is neglected, since there is nothing in the above proof to prevent our taking the structural unit larger than a single atom or molecule. One thus must attribute to crystalline imperfections, or some other deviation from perfect hexagonality, the variations of the Verdet constant within a plane perpendicular to the optic axis which are reported by Becquerel[5] in his noteworthy investigations on tysonite at low temperatures.

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        November 30, 1933.

[3] The utility of considering the partition function as a matrix spur in systems of representation which do not diagonalize the total energy has been stressed by F. Bloch, Zeits. f. Physik 74, 295 (1932); E. Wigner, Phys. Rev. 40, 749 (1932), R. Serber, ibid. 43, 1011 (1933). A development similar to (2) also has been utilized in Kramers' article on tysonite in Proc. Amsterdam Acad., 1933.

[4] For proof of (3) see J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Eq. (46) of Chapter VI, and (3) of Chapter VII. The quantum mechanical proof of (46) given in Section 36 was intended only for isotropic media, but is extended to crystals without difficulty by regarding W as a function of E_x, E_y, E_z rather than of just E.

[5] J. Becquerel, Leiden Comm. 211c.

Quantum Statistics of Almost Classical Assemblies*

It is the object of the present note to call attention to a slight error in Eqs. (10), (20) and (21) of an article of the same title, which appeared in a recent number of this journal,[1] and to make a few supplementary remarks. The right-hand side of each of these equations should contain an extra factor, $1/N!$. The origin of this factor will be apparent from the following considerations.

The sum of states of a real gas, consisting of N molecules, may be expressed in the form,

$$\sigma = \int_{-\infty}^{+\infty} \cdots \int \sum_n \psi_n^* e^{-\beta H} \psi_n dq_1 \cdots dq_{3N}, \tag{1}$$

where H is the Hamiltonian operator of the entire system, the ψ_n its characteristic functions, the q's are the configuration coordinates of the N molecules, and β is equal to $1/kT$. With the aid of the symmetric or the antisymmetric plane wave functions,

$$\Phi(p, q) = 1/(N!)^{\frac{1}{2}} \sum_P (\pm 1)^{|P|} \exp[(iP/h)\sum_{k=1}^{N} p_k \cdot r_k], \tag{2}$$

the orthogonal functions, ψ_n, may be expanded as Fourier integrals.

$$\psi_n(q) = \int_{-\infty}^{+\infty} \cdots \int S_n(p)\Phi(p, q)dp_1 \cdots dp_{3N}. \tag{3}$$

When these expansions are substituted in Eq. (1), one obtains,

$$\sigma = \int_{-\infty}^{+\infty} \cdots \int \{\sum_n S_n^*(p')S_n(p)\}\{\Phi^*(p', q)e^{-\beta H}\Phi(p, q)\}dp'_1 \cdots dp'_{3N}dp_1 \cdots dp_{3N}dq_1 \cdots dq_{3N}. \tag{4}$$

It may be shown without difficulty that functions, $S_n(p)$, which form a complete orthogonal set in momentum space, satisfy the following relation,

$$\sum_n S_n^*(p')S_n(p) = [1/N!(2\pi h)^N]\prod_{k=1}^{3N}\delta(p'_k - p_k), \tag{5}$$

where h is Planck's constant divided by 2π and $\delta(p' - p)$ is

[1] J. G. Kirkwood, Phys. Rev. 44, 31 (1933).

the Dirac delta-function. The error in the previous paper amounted to omitting the factor, $1/N!$, on the right-hand side of the above equation. The summation over the index, n, may be carried out with the aid of the completeness relation, Eq. (5), and the subsequent integrations over the $p'_1 \cdots p'_{3N}$, performed in the usual way.

$$\int_{-\infty}^{+\infty} F(p')\delta(p'-p)dp' = F(p). \qquad (6)$$

Finally, one obtains,

$$\sigma = [1/N!(2\pi h)^N] \int_{-\infty}^{+\infty} \cdots \int \Phi^*(p, q)e^{-\beta H}\Phi(p, q)dp_1 \\ \cdots dp_{3N}dq_1 \cdots dq_{3N}. \qquad (7)$$

This equation becomes identical with Eq. (10) of the previous article, except for the extra factor $1/N!$, when the functions $\Phi(p, q)$, given by Eq. (2) are explicitly introduced. Since Eqs. (20) and (21) are merely modifications of Eq. (10), they must also contain this factor. The same result is obtained when the completeness relation for the configuration wave functions, $\psi_n(q)$, is employed, instead of that of the momentum wave functions, $S_n(p)$.

The additional factor, $1/N!$, while relatively trivial from a mathematical point of view, is of considerable physical importance. When the right side of Eq. (7) is expanded in powers of Planck's constant, and only the first term is retained, one obtains the following semiclassical expression for σ.

$$\sigma = [1/N!(2\pi h)^N] \int_{-\infty}^{+\infty} \cdots \int e^{-\beta H(p, q)}dp_1 \\ \cdots dp_{3N}dq_1 \cdots dq_{3N}, \qquad (8)$$

where $H(p, q)$ is the classical Hamiltonian function. The entropy of the system is given by the usual formula,

$$S = k[\log \sigma - \beta(\partial \log \sigma/\partial \beta)]. \qquad (9)$$

Thus, the factor, $1/N!$, in σ provides the necessary term, $k(N - N \log N)$ in the entropy, after $\log N!$ has been approximated by Stirling's formula. In classical statistics, this factor, $1/N!$, has to be introduced somewhat arbitrarily. Gibbs accomplishes this by counting the group of $N!$ permutations or specific phases, included in each generic phase only once instead of $N!$ times. However, when classical statistics is treated as a limiting case of quantum statistics, the whole question is automatically taken care of by the symmetry restrictions imposed upon the wave functions by the Pauli exclusion principle.

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The Relative Abundance of the Lithium Isotopes

Although many attempts have been made to measure directly the relative abundance of the lithium isotopes the results so far reported are quite discordant. Bainbridge, in a paper describing his experiments on this problem,[1] has given a critical survey of the other work in this field. In this connection we thought it of interest to report the results of a set of experiments, extending over a period of several weeks, performed in connection with one of our laboratory courses.

A mass-spectrometer was constructed in the form of a glass tube bent in the shape of a semicircle having a filament and accelerating slit at one end and a slit and Faraday collector at the other. The walls of the tube were heavily silvered. The tube was surrounded by a solenoid capable of furnishing a magnetic field of 400 gauss. Lithium ions emitted by a spodumene coating on the filament described a semicircular path of 5.5 cm radius and those entering the collector were detected by means of an electrometer. The resolving power was sufficient to separate isotopes 6 and 7 quite well. The total emission from the filament was measured with a galvanometer. The conditions specified by Bainbridge,[1] that (1) the emission be not limited by space charge and (2) that ions reach the collector by identical paths, were fulfilled.

The results of a number of determinations for the current ratio Li^7/Li^6 all fell between 8 and 9 with an average value of 8.4. The results seemed to be independent of the current density within the errors of measurement and no change in the ratio with age of the filament was perceptible. Our results are in disagreement with those cited in reference (1) but agree with those of Wijk and Koeveringe[2] and Nakamura.[3] These authors found 7.2 and 8, respectively, from band spectra. All measured values are in bad agreement, however, with the abundance calculated from the masses of the isotopes and the atomic weight.

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December 12, 1933.

[1] K. T. Bainbridge, J. Frank. Inst. 212, 317 (1931).
[2] v. Wijk and v. Koeveringe, Proc. Roy. Soc. A132, 98 (1931).
[3] G. Nakamura, Nature 128, 759 (1931).

Multiple Laue Spots

Double Laue spots have been frequently observed when thick crystals composed of atoms of low atomic number were used. Cork[1] has described triple spots observed with crystals of quartz, calcite and Rochelle salt. A Laue photograph of a slab of crystalline quartz was recently made for the purpose of determining the directions of the

[1] Cork, Phys. Rev. 42, 749 (1932).