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RESEARCH MEMORANDUM

THERMODYNAMIC PROPERTIES OF MIXTURES ON THE STATISTICAL MODEL

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ABSTRACT

A new method of deriving Brachman's results for the thermodynamic functions of the Thomas-Fermi atom is given in a generalized form applicable to mixtures of electrons and light nuclei in the field of a heavy nucleus.

THERMODYNAMIC PROPERTIES OF MIXTURES ON THE STATISTICAL MODEL

Brachman[1] has described in outline a method for obtaining the general thermodynamic functions, in particular the Helmholtz free energy F, of the Thomas-Fermi atom at arbitrary temperature based on an integration of the Gibbs-Helmholtz equation. March[2] has pointed out that Brachman's result for the entropy follows directly from the Slater sum, using the distribution function appropriate to a gas of independent electrons at the given local electrostatic potential. In the present discussion we wish to present an alternative derivation of Brachman's results, in which the physical connection between F and the electron chemical potential μ_e occupies a central role, and which applies to somewhat more general systems.

The model to be considered consists of a central heavy nucleus of (large) atomic number Z, surrounded spherically by its complement of Z electrons plus n_s

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[1] M. K. Brachman, Phys. Rev. 84, 1263 (1951).

[2] N. H. March, Phil. Mag. 44, 346 (1953).

lighter nuclei (e.g., protons) of charge species z_s and their $n_s z_s$ electrons, the whole "molecular" unit being contained in a known spherical volume v at a given temperature T. The coordinate frame will be that of the central nucleus, which otherwise enters only as the source of an external field in which the electrons and the other nuclei move.

For simplicity we shall employ Fermi-Dirac statistics for all particles, writing[3] for the charge density ρ_s due to species s of chemical potential μ_s in a region where the total electrostatic potential is V

$$\rho_s = (z_s e g_s/h^3) \int_0^\infty \frac{4\pi p^2 dp}{\exp \beta(p^2/2m_s + z_s eV - \mu_s) + 1} = e z_s \lambda_s I_{1/2}\left[\beta(\mu_s - z_s eV)\right], \quad (1)$$

where g_s is the spin degeneracy $2S_s + 1$, $\beta = 1/kT$, $\lambda_s = 2\pi g_s (2m_s/\beta h^2)^{3/2}$ and

$$I_n(\eta) = \int_0^\infty y^n / \left[\exp(y-\eta) + 1\right] \cdot dy. \quad (2)$$

This is correct in any case for electrons, and makes little error even for boson nuclei as long as the temperature has the modest value required for the applicability of Boltzmann statistics. Except for the trivial difference in the assumed statistics, the model thus strongly resembles that of the familiar Debye-Huckel[4] description of ionic solutions, although the foregoing explicit form has been attributed[5] to L. Henyey and J. A. Wheeler.

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[3] cf. R. P. Feynman, N. Metropolis and E. Teller, Phys. Rev. 75, 1561 (1949), Sec. V.

[4] See, for example, R. Fowler and E. A. Guggenheim, Statistical Thermodynamics (Cambridge University Press, 1949), Chap. IX.

[5] A. Latter and R. Latter, "The Equation of State of Water on the Thomas-Fermi Model," J. Chem. Phys. (in press).

We begin by defining a class or homologous series of molecules (more exactly, molecular ions) in which the numbers n_s of particles of each species (except the invariant central nucleus) stand in constant ratio to one another. For example, the molecular ions consisting of the same central nucleus but surrounded by a) no electrons or protons b) two electrons and one proton c) four electrons and two protons, etc., all belong to the same class. Except for comparison with experiment we need not limit our considerations to integral numbers of particles, in which case we may distinguish the members of a given class by a continuous parameter Θ on the interval (0, 1):

$$n_s = \Theta N_s. \tag{3}$$

The plan will be to assemble the desired final neutral molecule, $\Theta = 1$, whose composition is specified by the central nuclear charge Z and the N_s, by progressing up the homologous series. From the combined first and second laws of thermodynamics, the differential of the Helmholtz free energy is

$$dF = - SdT - pdv + \sum \mu_s dn_s. \tag{4}$$

Thus, if the process of assembly is carried out at constant temperature and volume,

$$F = \sum \int_0^{N_s} \mu_s dn_s = \sum \mu_s N_s - \sum \int n_s d\mu_s, \tag{5}$$

in which the constant of integration, corresponding to the free energy of the bare central nucleus, has been set equal to zero. Evidently one needs to know only how n_s depends upon μ_s, or how each depends on Θ.

Denoting the potential energy of interaction between the nucleus and the given distribution of species s by U_{sn}, and between the distributions of species s and t by U_{st}, we have

$$U_{sn} = \int \rho_s V_n \, d\tau, \qquad (1+\delta_{st}) U_{st} = \int \rho_s V_t \, d\tau, \tag{6}$$

where V_n is the electrostatic potential due to the nucleus, and V_t that due to the distribution ρ_t. We thus write the potential energy of interaction of the charge distribution with itself as

$$U - \sum_s U_{sn} = \sum_{s \geq t} \sum U_{st} = (1/2) \int \rho (V - V_n) d\tau, \tag{7}$$

where the total charge density is $\rho = \sum \rho_s$.

The total kinetic energy is given by[3]

$$T = \sum_s (\alpha_s/\beta) \int I_{3/2} [\beta(\mu_s - z_s e V)] \, d\tau. \tag{8}$$

If we now form the combination $(2T/3 + \sum\sum U_{st})$ and differentiate with respect to Θ, noting from (2) that $I'_{n+1}(\eta) = (n+1) I_n(\eta)$, we find

$$\partial(2T/3 + \sum\sum U_{st})/\partial\Theta = \sum_s n_s \partial\mu_s/\partial\Theta + (1/2) \int \left[(\partial\rho/\partial\Theta)(V - V_n) - \rho \partial(V - V_n)/\partial\Theta \right] d\tau.$$

By the application of Green's theorem, the integral is easily brought into the form

$$-(1/8\pi) \oint (V - V_n)^2 \partial \left[\underset{\sim}{\nabla} \ln (V - V_n) \right] / \partial\Theta \cdot d\underset{\sim}{S}.$$

For any Θ, the electric field at the boundary of the molecular ion is continuous across the surface, since there is no surface charge. Outside this

(spherical) surface, $(V-V_n) = (\sum n_s z_s e)/r$, so that the gradient of the logarithm of this quantity is independent of Θ at the boundary, and the integral vanishes, leaving

$$\sum n_s \partial\mu_s/\partial\Theta = \partial(2T/3 + \sum\sum U_{st})/\partial\Theta. \qquad (9)$$

Insertion of this expression into Eq. (5) now gives for the Helmholtz free energy

$$F = \sum_s \mu_s N_s - 2T/3 - \sum_{s \geq t}\sum U_{st}. \qquad (10)$$

This correctly reduces to Brachman's expression when only a single species (namely electrons) is present, and agrees with the result of March's method extended to the multicomponent system.

It is now clear that the special properties of the assumed homologous series nowhere enter the derivation. Any process of assembly could have been used provided only that it is conducted at constant temperature and volume. It is felt, however, that the retention of this artifice makes the motivation a little clearer. Finally, it is to be noted that Eq. (10) applies equally well to ions as to the neutral aggregate.