Some Critical Remarks Concerning Bailli Nilsen's Paper: ``On the Theory of Free Radicals and OrganoAlkali Compounds''

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the direct use of our expressions for the chemical potentials being the most obvious. An alternative and more phenomenological treatment applicable to dilute solutions has also been undertaken. These investigations will be described in a future article.

Note added in proof:

(a) A remark about the normalization of the molecular pair distribution functions is perhaps worth while. In defining the potential of mean force, $W_i{}^k(\lambda_i)$, an arbitrary constant is at our disposal. This constant has been so chosen that

$$(1/v\sigma_k)\int e^{-\beta W_i{}^k(\lambda_i)}d\omega_k = 1$$

a relation which may be verified by reference to Eq. (20b). The approximate forms for $W_i{}^k(\lambda_i)$ of course do not exactly satisfy this condition.

(b) At sufficiently high temperatures, the exponentials of Eq. (41) may be expanded and the following approximate linear integral equation is obtained

$$W_i{}^k(\lambda_i) = \lambda_i V_{ik} - \frac{\lambda_i}{kT}\sum_s \frac{N_s}{v}\frac{1}{\sigma_s}\int V_{is}W_k{}^s(1)d\omega_s$$

where regions in which $W_i{}^s$ and $W_k{}^s$ become infinite due to repulsive forces, are excluded from the integration. If we apply the equation to the ions of an electrolyte solution, the solvent being treated as a continuous medium of dielectric constant D, we know that V_{ik} is equal e_ie_k/Dr_{ik} where e_i and e_k are the ionic charges. For this potential, it may be verified without difficulty that the above set of linear integral equations has the following solutions

$$W_i{}^k(\lambda_i) = \lambda_i \frac{e_ie_k}{Dr_{ik}}e^{-\kappa r}{}_{ik}; \qquad \kappa^2 = \frac{4\pi}{DkT}\sum_s \frac{N_s}{v}e_s{}^2$$

if molecular size is neglected. These solutions, together with Eq. (22) lead to the Debye-Hückel limiting law for the chemical potentials of the ions.

Some Critical Remarks Concerning Bailli Nilsen's Paper: "On the Theory of Free Radicals and Organo-Alkali Compounds[1]" *

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LATELY, a paper by Bailli Nilsen on the above title appeared in this journal, the main subject of the article being a computation of the electron affinities of free aromatic radicals.

The author first mentions two possible ways of a quantum-mechanical calculation of the electron affinities of such free radicals,—the "first method" certainly alluding to some ordinary first order perturbation method for an atom, or, a molecule when adding an extra electron on an unoccupied orbit—whereas the "second method," as he says, is closely connected with Pauling and Wheland's theory for free radicals.

If now, for instance, we apply such an ordinary perturbation method to the simplest of all atoms, the hydrogen atom, we will find a very poor approximate value of the electron affinity—even the sign being wrong—*viz.*, the negative value -0.25 Rh or -3.385 electron volts—whereas an exact calculation provides a positive value 0.0506 Rh or 0.685 electron volt.

It is true, therefore, that there are many difficulties in determining the energy difference caused by putting an extra electron into an atom or a molecule. We also know that these difficulties are closely connected with considerable changes of the electronic configuration of the atom, because the electron orbits are deformed by the mutual interaction of the electrons. These changes can only be accounted for by the aid of complicated variational methods.

The author of the above paper now seems to be of the opinion that such difficulties may be conquered simply by dropping them out of sight and by making use of the essentially different "second method" of Pauling and Wheland, which is especially suited for quite other purposes, *viz.*, the computation of binding forces between atoms of **given electronic configurations.**

We will, however, quite overlook the considerable errors introduced in this way by neglecting energy changes in the individual atoms themselves, and only analyze the author's application of the "second method."

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In Pauling and Wheland's paper electron orbits in individual atoms are designated by letters $a, b, c, \cdots$ and exchange integrals between such orbits by ab, ac, bc, etc. The exchange integrals are, therefore, mathematically well-defined quantities depending only upon the geometrical properties of the supposed electron orbits, which may, for instance, be expressed by some definite kind of eigenfunctions. The values of the integrals have nothing at all to do with the binding electrons occupying those orbits, they only enter into the secular equation of the problem on account of the presence of such electrons.

Now Pauling and Wheland in dealing with the seven-electron problem of the benzyl radical, formally add an eighth electron, called "phantom electron," and a corresponding "phantom orbit" h. Equating to zero all exchange integrals between real orbits and the "phantom orbit" they get a number of singlet terms corresponding exactly to the number of doublet terms of the real problem and with the same energy values.

This procedure may be considered as a purely formal trick, but we may also imagine that it has a definite physical meaning. The "phantom orbit" may well be interpreted as a real electron orbit in a second molecule at some distance which allows the exchange integrals mentioned to be put approximately equal to zero, thus giving qualitatively a picture of a faint, although real and active valence force pointing from the free radical under consideration to some second distant atom or molecule.

In Bailli Nilsen's paper, however, there is no clear distinction between the binding electrons themselves and the possible orbits of the electrons. Sometimes he speaks of exchange integrals between orbits, sometimes between electrons, and he never tries to give a clear definition of the "phantom orbit" introduced. On the contrary he only speaks of the "partner" of the "charging electron" in that or that "canonical structure." Following Pauling and Wheland he assigns definite values to the exchange integrals $ab, ac, \cdots$, $bc, bd \cdots$, between the 7 original orbits, $a, \cdots g$, either the common approximate value α or the

approximate value zero according to whether the orbits belong to neighboring atoms or not. In this case he quite correctly takes no account of the direction of the valence forces in various "canonical structures." In the case of the "phantom orbit," however, **he puts the exchange integrals ah, bh, ch, etc., sometimes equal to α and sometimes equal to zero—in the very same secular equation.**

Thus in his matrix element H_{11} we have to add integrals of this kind to the complete expression

$$-\tfrac{1}{2}(ah+bh+ch+dh+eh+fh)+gh$$

and correspondingly in his matrix element H_{35} we get the expression

$$\tfrac{1}{2}[ah+ch-2\,bh-\tfrac{1}{2}(dh+eh+fh+gh)].$$

In the first matrix element H_{11} he now puts $gh=\alpha$, all other integrals equal to zero, whereas in the second element H_{35} he assigns the value α to ah and ch now putting all remaining integrals, including the above gh, equal to zero.

Having completely overlooked the necessity of a "materialization" of the "phantom orbit" he can freely fancy that his "phantom electron" is sometimes here and sometimes there, in the "neighborhood" of this or that "partner."

If it had originally been the author's opinion that the "charging electron" is in some way continually jumping from one atom of the molecule to another, he should, or course, have made use of the available electron orbits, one per atom. Then there would be a different number of orbits and electrons, and the special formal method of "superposition patterns" put forth by Pauling and Wheland could not have been applied at all in the given form. Also in this case, of course, the difficulties of determining the perturbation energy of the individual atoms remain to the same degree.

The conclusion I want to give is, therefore, that in my opinion the whole treatment of the electron affinities of free aromatic radicals as given by Bailli Nilsen is unclear and misleading—and if not thoroughly revised—it must be considered as meaningless.