$$K = \frac{P_B}{P_A} = \frac{t_B}{t_A}$$

where t_A and t_B are the lifetimes of the A and B forms.

In the limit of rapid exchange, the observed sodium splitting, $\bar{a}$, is given by

$$\bar{a} = P_A a_A + P_B a_B = \frac{a_A + K a_B}{1 + K} \quad (1)$$

The contribution of the exchange to the line width of the sodium line can be determined by the standard procedure.[8]

$$\left(\frac{1}{T_2}\right)_{ex} = P_A{}^2 P_B{}^2 (W_A - W_B)^2 t_A (1 + K) \quad (2)$$

In this equation W_A and W_B represent the resonant frequencies of the two types of ion pairs considered.

Values of K were determined for various temperatures through use of eq 1. We estimated the values of a_A and a_B to be 1.55 gauss and 0, respectively, for both systems under consideration. These values were obtained by extrapolating to the high- and low-temperature limits of the sharp fall-off region. The equilibrium between A and B is thought to be between tightly associated ion pairs, A, and loosely associated ion pairs, B.

A plot of log K *vs.* $1/T$ yields satisfactory straight lines for both systems. The slope of the lines gives $\Delta H = -4.5$ kcal for the anthracene case and -4.6 kcal for the di-*t*-butylnaphthalene case. The entropy change was estimated to be -22 eu for the anthracene case and -21 eu for the di-*t*-butylnaphthalene case.

The end of the epr spectrum of anthracene, at various temperatures, is shown in Figure 2 along with stick diagrams which show the position and relative intensities of the lines. Analogous results were obtained for di-*t*-butylnaphthalene. It is seen that at lower temperatures the line width depends on the magnetic quantum number of the sodium nucleus, $M_Z{}^{NA}$. Peaks with $M_Z{}^{NA} = \pm {}^3/_2$ broaden more rapidly than peaks with $M_Z{}^{NA} = \pm {}^1/_2$. Since $W_A - W_B$ is ${}^3/_2 \cdot a_A\gamma$ for peaks with $M_Z{}^{NA} = \pm {}^3/_2$ and ${}^1/_2 a_A\gamma$ for peaks with $M_Z{}^{NA} = \pm {}^1/_2$, this variation in line width is expected when the rate of conversion between A and B approaches the hyperfine frequency.

Through the use of eq 2, we have analyzed our data to give estimates of the lifetimes of species A and B. At $-55°$, t_A and t_B are 1×10^{-8} and 3×10^{-9} sec, respectively, for the anthracene case and 4×10^{-8} and 2×10^{-8} sec for the di-*t*-butylnaphthalene case.

The values of ΔH and ΔS obtained are similar in magnitude to those estimated for the dissociation of the sodium naphthalide ion pair. A similar discussion to that given in ref 2 can be used to explain these values. A large negative entropy change indicates a higher degree of ordering of solvent molecules in form B than in form A.

A rapid equilibrium between ion pairs and free ions cannot explain our observations, as rapid interchanges of different sodium nuclei would broaden out the metal splitting. We observe the spectra of the free ion as well, showing that a second equilibria between ion pairs and free ion is present.[2]

We feel that the linear change of log K with the reciprocal of temperature and the alteration in line widths strongly support the described mechanism. We are presently unwilling to commit ourselves on the mechanism leading to the slow increase in the sodium coupling constant in 2,6-di-*t*-butylnaphthalene at higher temperatures; however, we feel that slight changes in the structure of the tight ion pair could account for this variation. The presence of a second weakly associated ion pair may also account for Reddoch's[9] observations of slight changes in the proton coupling constants, upon dilution, in the anthracene radical anion.

Detailed studies on the structure and equilibria involving ion pairs and their connection to the kinetics of rapid electron-transfer reactions are now in progress and will be reported later.

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(9) A. H. Reddoch, *J. Chem. Phys.*, **43**, 225 (1965).

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The Fluorides and Oxides of Helium and Neon[1]

Sir:

High-accuracy, many-electron, valence-bond wave functions have been obtained for HeO, HeF, NeO, NeF, and NeF_2. As shown in Figure 1, the potential energy curves for all of these species are repulsive (for NeF_2 and HeF_2 the linear molecule in a symmetric stretch is plotted). The method of forming the wave functions is the same as that previously reported for HeF_2,[2] and the NeF_2 result represents the highest precision quantum-mechanical solution yet achieved for a molecular system with this number of electrons.

The existence of HeO has been predicted by Jørgensen,[3] and Noyes[4] has predicted NeO and NeF. Their work employs reasonable and accepted chemical arguments. Considerable effort has been expended on attempts at the synthesis of HeF_2 and NeF_2 by a number of laboratories. It is also interesting to note that while the repulsive potential surfaces of Figure 1 can be roughly related to the high ionization potentials of helium and neon, the ordering of the curves does not follow the ordering of the ionization potentials (or electronegativities) of the participating atoms. All of these research efforts illustrate the general paucity and desirability of truly quantitative electronic structure calculations for much of chemistry.

The valence-bond wave functions have been constructed using the exact Hamiltonian with simultaneous

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(1) This work has been supported by the Chemistry Programs Section of the U. S. Atomic Energy Commission Research Division.

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(4) R. M. Noyes, *J. Am. Chem. Soc.*, **85**, 2202 (1963). This article also suggests that HeH might be observed. A very precise wave function leading to a repulsive potential energy curve for this molecule has been obtained by H. S. Taylor and F. E. Harris, *Mol. Phys.*, **7**, 287 (1963).

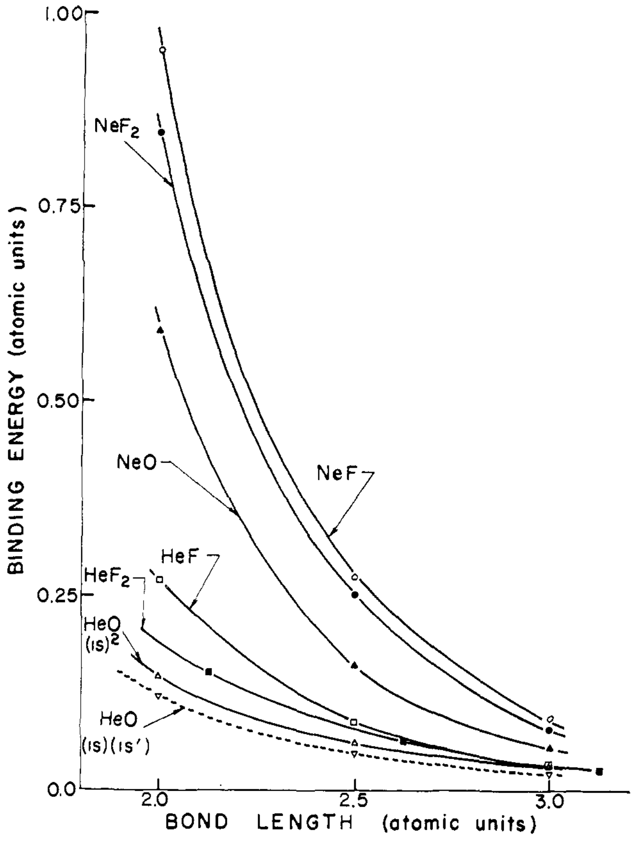

Figure 1. Average bond energies *vs.* bond length.

inclusion of all the electrons. A complete configuration interaction over the occupied atomic orbitals was carried out for each molecule with a Hartree–Fock atomic basis set. Thus the NeO wave function includes the chemical structures NeO, Ne^+O^-, $Ne^{2+}O^{2-}$, and is composed of 16 states made up from twenty-four 18 × 18 determinants. The curves of Figure 1 are all singlets with the oxygen atoms going to a ^1D configuration at infinite separation. Triplet states for the oxides were calculated. For these the free oxygen atom is in its ground-state ^3P configuration (calculated to be 0.0805 au lower than the ^1D), but the molecular potential energy curves lie even higher than the corresponding fluorides. Table I displays the chemically significant terms in the wave functions for the various species. The fact that the neon-associated species lie above those with helium can be attributed simply to the relative size of these atoms, although it is difficult to assign an effective radius to helium or bond length for HeO or HeF (the leading term in the wave functions effectively represents two neutral atoms repelling one another, and its coefficient measures the extent to which they have achieved a free atom-like behavior). As would be expected, the triatomic bifluorides lie below the diatomic fluorides because their extra symmetry element leads to resonance. The particularly interesting result showing the oxides to lie lower in energy than the fluorides arises from three factors which together override the greater electronegativity of fluorine. In the *neutral* states 2s–2p hybridization, favored in oxygen over fluorine because of the smaller orbital energy separation, together with the existence of half-filled π orbitals in the oxygen-containing species permits an energy lowering charge redistribution. Hybridization in these states allows the charge to move away from the between atom-repulsive region. Among the *singly ionized* states there are three in NeO and one in HeO which significantly lower the energy through formation of electron-pair bonds between open shells on each atom. Hybridization in the ionic states has the opposite sense to that in the neutral states, favoring the pair bonds by building up the charge between atoms. Purely ionic contributions are almost identical for both the fluorides and oxides, and the doubly ionized states, possible for the oxides but not the fluorides, make such an insignificant contribution that they have been omitted from the approximate wave function tabulation in Table I. In general, binding is discouraged because in the dominant states one of the atoms always has a closed-shell configuration. Since HeO exhibited the least repulsion, an even more elaborate configuration interaction, including different orbitals for different spins on helium, was carried out with the result shown by the dotted curve in Figure 1.

Table I. Wave Functions at 2.0 au (1.06 A)

HeO	$\Psi \cong +0.714\mathrm{HeO}(2s)^2(2p_\pi)^4 - 0.072\mathrm{HeO}(2s)(2p_\sigma)(2p_\pi)^4 - 0.071\mathrm{HeO}(2p)^6 - 0.051\mathrm{HeO}(2s)^2(2p_\sigma)^2(2p_\pi)^2 + 0.377\mathrm{He^+O^-}(2s)^2(2p_\sigma)(2p_\pi)^4$
NeO	$\Psi \cong +0.600\mathrm{NeO}(2s)^2(2p_\pi)^4 - 0.157\mathrm{NeO}(2s)(2p_\sigma)(2p_\pi)^4 - 0.037\mathrm{NeO}(2p)^6 - 0.031\mathrm{NeO}(2s)^2(2p_\sigma)^2(2p_\pi)^2 - 0.364\mathrm{Ne^+}(2s)^2(2p_\sigma)(2p_\pi)^4\mathrm{O^-}(2s)^2(2p_\sigma)(2p_\pi)^4 - 0.107\mathrm{Ne^+}(2s)(2p)^6\mathrm{O^-}(2s)^2(2p_\sigma)(2p_\pi)^4 + 0.043\mathrm{Ne^+}(2s)^2(2p_\sigma)(2p_\pi)^4\mathrm{O^-}(2s)(2p)^6$
HeF	$\Psi \cong +0.848\mathrm{HeF}(2s)^2(2p_\sigma)(2p_\pi)^4 + 0.282\mathrm{He^+F^-}$
NeF	$\Psi \cong +0.770\mathrm{MeF}(2s)^2(2p_\sigma)(2p_\pi)^4 - 0.360\mathrm{Ne^+}(2s)^2(2p_\sigma)(2p_\pi)^4\mathrm{F^-} + 0.104\mathrm{Ne^+}(2s)(2p)^6\mathrm{F^-}$

For argon the one-electron orbital energies of the 3p and 3s are remarkably close to degeneracy with the O 2p and O 2s, respectively. This renders simple electronegativity arguments ineffective, but our quantitative numerical experience with neon and helium suggests that the strong mixing of these states may produce minima in the potential energy surfaces for ArO_3 and ArO_4. For these and the fluorides ArF_2, and ArF_4, it is decidedly a border-line case as to whether or not they will show potential minima, and from a theoretical viewpoint it will require wave functions of the present degree of sophistication to provide a convincing answer. Such calculations are under way in this laboratory. The present massive synthesis effort for helium, neon-, and argon-containing species will provide a rigorous experimental test of the theory.

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Crystal Structure Studies of Some Unusual Antimony Bromide Salts[1]

Sir:

The group of salts of the type R_2SbX_6 ($R = NH_4^+$, Rb^+, or Cs^+; X = Cl or Br) has been the subject of con-

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