[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

The Electronic Structure of Hydrogen Fluoride[1]

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A self-consistent field calculation of the normal state of HF in the molecular orbital(MO) approximation is made. The molecular orbitals(MOs) are expressed as linear combinations of all valence and inner shell atomic orbitals of the atoms, and all interactions of the ten electrons are included. The MO functions are used to compute the dissociation energy and dipole moment of the molecule. An equivalent orbital representation is obtained by an orthonormal transformation of the MOs which shows definite directional features of the distribution of electron density. The latter is discussed briefly in connection with the dipole moment and with association in HF.

The structure of a number of simple molecules, including HF, has been treated recently by a method of equivalent orbitals.[2] In HF, the lone pair electrons were assigned to three equivalent orbitals, which were represented by $s - p$ hybridized functions directed in three azimuthal planes at angles of 120° to each other. Orthogonality between the lone pair functions requires that the angle between the axis of a lone pair function and the bond axis should be greater than 90°, but the actual angle could not be determined. Consequently the angle between the lone pair axes is not known, and only tentative conclusions could be drawn concerning the electron density distribution in the lone pair region of the molecule.

Equivalent orbitals are derived from molecular orbitals(MOs), by orthonormal transformations,[3] and if a good (or the best) set of MOs is known, the lone pair distribution, and its contribution to the dipole moment of HF can be discussed more precisely. The purpose of the present calculations was to find such MOs by a self-consistent-field (SCF) procedure. In this calculation, all ten electrons have been assigned to MOs and all interactions have been included. Thus the importance of inner-shell–outer-shell mixing can be assessed, as has been done in a recent calculation on the water molecule.[4] Other theoretical calculations on HF have been made by Mueller,[5] who used a limited MO treatment as well as an atomic orbital method and a method of semi-localized orbitals. An elaborate valency bond treatment of HF has been published recently by Kastler.[6]

Method of Calculation.—HF has a closed-shell ground state, with five doubly occupied MOs, and the method described by Roothaan[7] may be applied directly. The MOs are expressed as linear combinations of atomic orbitals

$$\phi_i = \sum_p a_{ip}\chi_p \qquad (1)$$

The χ_p are specifically f, h, s, z, x, y, defined as

$$\begin{aligned} h &= (1s)_H = (1/\pi)^{1/2}\exp(-r_H) \\ f &= (1s)_F = (c_1^3/\pi)^{1/2}\exp(-c_1r_F) \\ s &= 1.02951(2s)_F - 0.244726(1s)_F \\ &[(2s)_F = (c_2^5/3\pi)^{1/2}r_F\exp(-c_2r_F)] \end{aligned} \qquad (2)$$

$$\left.\begin{matrix} z \\ x \\ y \end{matrix}\right\} = \left.\begin{matrix} (2p_z)_F \\ (2p_x)_F \\ (2p_y)_F \end{matrix}\right\} = (c_2^5/\pi)r_F\exp(-c_2r_F) \left\{\begin{matrix} \cos\theta \\ \sin\theta\cos\phi \\ \sin\theta\sin\phi \end{matrix}\right.$$

$$c_1 = 8.7;\ c_2 = 2.6$$

The orbital $(2s)_F$ is not used directly in the calculation; only the orthogonalized form s is used. The normalized ten-electron wave function of the normal state is an antisymmetrized product of the functions (1). The requirement that the energy corresponding to this state function shall be an absolute minimum leads to the matrix equations

$$(\mathbf{H} + \mathbf{G})\mathbf{a}_i = \epsilon_i\mathbf{S}\mathbf{a}_i \qquad (3)$$

H, **G** and **S** in the present case are 6 × 6 matrices, while the $\mathbf{a}_i$ are vectors, which are column matrices of the coefficients of the atomic orbitals in the ϕ_i of equation 1. The matrices **H**, **G** and **S** are made of elements of the operators H, G and unity, evaluated over the atomic orbitals (2). The definitions of these operators have been given in detail,[7,8] and will not be repeated here. The equation 3 is to be satisfied simultaneously by a set of (six) $\mathbf{a}_i$ and corresponding eigenvalues ϵ_i. An iterative method of solution is required, since the elements of **G** depend on the $\mathbf{a}_i$. Molecular symmetry ($C_{\infty v}$ here) is used to reduce the matrix equation 3 into one set of four equations for the A_1 orbitals and into two identical equations for the E orbitals. The molecular orbitals of proper symmetry are

(A_1 Orbitals)

$$\begin{aligned} \phi_1 &= a_{11}h + a_{12}f + a_{13}s + a_{14}z \\ \phi_2 &= a_{21}h + a_{22}f + a_{23}s + a_{24}z \\ \phi_3 &= a_{31}h + a_{32}f + a_{33}s + a_{34}z \\ \phi_6 &= a_{61}h + a_{62}f + a_{63}s + a_{64}z \end{aligned}$$

(ϕ_6 is not occupied in the ground state)

(E orbitals)

$$\phi_4 = x$$
$$\phi_5 = y$$

The secular equations for the A_1 orbitals were solved for the orbital energies and coefficients by the method of James and Coolidge.[9] The final values of the coefficients are shown in equations 5, where numbers in parentheses show values of coefficients introduced before the final solution. The orbital energies are given in Table I. The coefficients in (5) and corresponding ϕ_i are referred

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[1] Acknowledgment is made to the Office of Ordnance Research, U. S. Army, which supported this work in part under Contract DA-30-115-ORD-295 with the University of Rochester.

[2] A. B. F. Duncan and J. A. Pople, *Trans. Faraday Soc.*, **49**, 217 (1953).

[3] J. E. Lennard-Jones, *Proc. Roy. Soc.* (*London*), **A198**, 14 (1949).

[4] F. O. Ellison and H. Shull, *J. Chem. Phys.*, **21**, 1420 (1953).

[5] C. R. Mueller, *ibid.*, **19**, 1498 (1951).

[6] D. Kastler, *J. chim. phys.*, **50**, 556 (1953).

[7] C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951). A recent treatment of the CO molecule by this method has been made by R. C. Sahni, *Trans. Faraday Soc.*, **49**, 1246 (1953).

[8] J. F. Mulligan, *J. Chem. Phys.*, **19**, 347 (1951).

[9] H. M. James and A. S. Coolidge, *ibid.*, **1**, 825 (1933).

to as exact solutions. Actually the equations were solved first with the simplifying assumption of no inner–outer shell mixing, with $a_{32} = 1$ and a_{12}, a_{22}, a_{33} and $a_{34} = 0$. These solutions are referred to as approximate. The approximate functions ϕ_i^a derived on this assumption are shown in equations 6 and the corresponding eigenvalues are shown in Table I.

$$\left.\begin{array}{l} \phi_1 = 0.3850h - 0.03503f + 0.7400s + 0.1048z \\ \qquad (0.3852) \quad (0.03504) \quad (0.7398) \quad (0.1051) \\ \phi_2 = 0.1743h - 0.005702f - 0.3588s + 0.8980z \\ \qquad (0.1734) \quad (0.005652) \quad (0.3586) \quad (0.8983) \\ \phi_3 = -0.004916h + 1.00012f + 0.01877s + 0.002946z \\ \qquad (0.004919) \quad (1.00012) \quad (0.01877) \quad (0.002945) \\ \phi_6 = -1.1326h + 0.05271f + 0.8060s + 0.5598z \end{array}\right\} \tag{5}$$

$$\begin{array}{l} \phi_1^a = 0.4054h + 0.7246s + 0.09722z \\ \qquad (0.4055) \quad (0.7244) \quad (0.09746) \\ \phi_2^a = 0.1779h - 0.3644s + 0.8953z \\ \qquad (0.1771) \quad (0.3641) \quad (0.8956) \\ \phi_3^a = f \\ \phi_6^a = -1.1221h + 0.8168s + 0.5650z \end{array} \tag{6}$$

TABLE I

CALCULATED ENERGY VALUES

(in units $e^2/a_0 = 27.205$ e.v., except where noted)

Orbital energies ϵ_i (of ϕ_i)	Exact values	Approximate values
ϵ_1	−1.5688	−1.6066
ϵ_2	−0.5396	−0.5576
ϵ_3	−25.9859	−26.0171
$\epsilon_4 = \epsilon_5$	−0.4156	−0.4334
ϵ_6	+1.1822	+1.1032
$(\epsilon_1 + \epsilon_2 + \epsilon_3 + 2\epsilon_4)$	−28.9255	−29.0481
Total electronic energy (E)	−104.9037	−104.9557
Nuclear repulsion energy (E_n)	+5.1939	+5.1939
Total molecular energy	−99.7098	−99.7618
Energy of separated atoms	−99.4700	−99.4700
D_e	0.2398	0.2918
	(6.52 e.v.)	(7.94 e.v.)
D_e (exptl.)	$\leqq 0.2446\ e^2/a_0$	$\leqq 6.66$ e.v.

The self-consistency of the results is seen better by the fact that the final total molecular energy is only about 0.001% lower than in the preceding trial; the corresponding increase in dissociation energy is about 0.05%.

Total Energy and Dissociation Energy.—The total energy of the ground state is (in atomic units)

$$E_{\text{total}} = E + E_n; \; E_n = Z_F Z_H / r_{(H-F)}$$

where E is the total energy of the electrons. E may be expressed as[10]

$$E = 2\sum_i H_i + \sum_{ij} (2J_{ij} - K_{ij}) \tag{7}$$

The orbital energies ϵ_i satisfy the equation

$$H_i + \sum_j (2J_{ij} - K_{ij}) = \epsilon_i$$

from which

$$E = \sum_i H_i + \sum_i \epsilon_i = \sum_i \int \phi_i H \phi_i \, dv + \sum_i \epsilon_i$$

The values of $\sum\limits_i \epsilon_i$, E, and E_n are shown in Table I for the exact and approximate solutions. The energy of the F atom was calculated with the same atomic orbitals which were used in the molecular calculation. The energy of the H atom was added to get the energy of the separated atoms, each in its normal state. The difference between this sum and the total molecular energy is the dissociation energy, D_e, which is found to be 6.52 e.v. in the exact treatment and 7.94 e.v. in the approximate treatment. The experimental result is D_e = 6.66 e.v., which is obtained by addition of the zero point energy to D^0_0 = 6.40 e.v.[11]

The effect of inner–outer shell mixing is shown clearly in the result that the total energy is lower in the approximate treatment than in the exact treatment. In the exact treatment the calculated dissociation energy is better than might be expected. In the approximate treatment, however, the calculated dissociation energy is somewhat higher than the experimental value. Two comments may be made on this unexpected result. While the functions (5) obtained from the exact treatment are strictly orthogonal, there is an appreciable lack of orthogonality between ϕ^a_3 and the other functions (6). It may be noted also that the calculated energy of the F atom (−98.9700 e^2/a_0) is appreciably higher than an experimental value (−99.76 e^2/a_0) obtained from successive ionization potentials.[12] The experimental value of the energy of the separated atoms is thus −100.26 e^2/a_0, or 0.79 atomic unit lower than was calculated. Possibly the reason for this lies not so much in the atomic functions themselves, but in the large Coulomb repulsion of the electrons. A similar situation must exist in the molecular case, which leads to the conclusion that the total molecular energy should be somewhat lower than has been calculated, both in the exact and approximate treatments. It is difficult to estimate the relative repulsion in the atomic and molecular cases and the over-all effect on the dissociation energy. Since the latter is only about 0.4% of the total molecular energy, perhaps only an agreement in order of magnitude is to be expected for the dissociation energy.

Ionization and Excitation Energies in HF.—The negatives of the orbital energies form a good approximation to the ionization potentials of the molecule.[7] Unfortunately there are no known experimental values for HF. Theoretically, the lowest potential is expected (and found) to be that of ϕ_4 (or $2p_x$) = 11.3 e.v. This is considerably lower than the corresponding potential in the F atom (17.42 e.v.).[12] But it is questionable whether such a comparison should be made. The repulsions of the H atom and perhaps an excessive repulsion by the other electrons in x and y orbitals contribute large positive values to the matrix element which determines the orbital energy of x. This matrix element, and consequently the potential, is smaller than it would be in the free atom. The other calculated ionization potentials appear to have reasonable values.

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[10] See ref. 6, equations 20–26, 31, and unnumbered equations between equations 64 and 65.

[11] G. Herzberg, "Molecular Structure and Spectra. I. Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1950, p. 5136.

[12] C. E. Moore, "Atomic Energy Levels," Vol. I, Nat. Bur. Standards, Circ. 467, U. S. Department of Commerce, Washington, 1949.

The lower energy electronic transitions in HF result probably from excitation of an electron from a ϕ_4 (x) orbital, possibly to *ns* and *nd* atom like orbitals. Excitation to the antibonding orbital ϕ_6 can occur evidently only at very high energies. The experimental data from ultraviolet absorption spectra are meager, are extremely difficult to obtain, and are complicated by association at the pressures and temperatures necessary to obtain adequate absorption.[13] Absorption appears to begin at about 55000 cm.$^{-1}$ (6.0 e.v.) with indication of a maximum at 62000 cm.$^{-1}$ (7.69 e.v.) at 100–165°. If this absorption corresponds to an orbital excitation $2p_x \rightarrow 3s$, then the term value of $3s$ in HF is about 40450 cm.$^{-1}$. The term value of $3s$ in the F atom is at about 36000 cm.$^{-1}$.

Dipole Moment and Electron Distribution.—The total dipole moment M (in Debye units (D)) is

$$M = -2ea_0 \sum_{i=1}^{5} \int \phi_i \mathbf{r} \phi_i \, dv + ea_0 \sum_{n} Z_n \mathbf{r}_n$$

where $\mathbf{r}$ and $\mathbf{r}_n$ are, respectively, the vector distances in atomic units of an electron and a nucleus from the origin of a suitable coördinate system. Here the origin is taken at the F atom and the positive z direction extends along the internuclear axis or bond line toward the H atom. The total moment will have a positive resultant value in the positive z direction; in this direction the individual moments in the first summation may have positive or negative signs, depending on the wave functions. The resultant dipole moment M calculated with the set of functions (5) is 2.65 D and with the approximate functions (6) is 2.53 D. Consequently there is no improvement in the calculation by the inclusion of $(1s)_F$ mixing. This is in contrast to the results of Ellison and Shull[4] on the water molecule. The calculated values are about 33–39% higher than the experimental value (1.91 D). It may be pointed out, however, that this calculation is extremely sensitive to the coefficients in the functions used. The values are about equal to values reported by Kastler,[6] but are inferior to Mueller's value from semi-localized orbitals.

An analysis of the contributions of the individual moments of the different electron distributions to the total moment is shown in Table II, together with the moment arising from the nuclei. It is apparent that the moment of the distribution $|\phi_1|^2$ is negative in the direction of the total moment, as would be expected from the bonding character of this molecular orbital. The moment of the distribution $|\phi_2|^2$ has the opposite sign, which indicates that this distribution is directed away somewhat from the bond direction. The functions ϕ_1 and ϕ_2 (ϕ_1^a and ϕ_2^a) are not sufficiently localized, however, to be described, respectively, as bonding and lone pair functions. But if these molecular orbitals are subjected to the orthogonal transformation

$$\begin{aligned} \phi_1' &= \phi_2 \cos \lambda + \phi_1 \sin \lambda \\ \phi_2' &= -\phi_2 \sin \lambda + \phi_1 \cos \lambda \end{aligned} \tag{8}$$

and if λ is adjusted to make a_{21} vanish, there is obtained the following sets of MOs

$$\begin{aligned} \phi_1' &= 0.4226h - 0.3426f + 0.5262s + 0.4658z \\ \phi_2' &= -0.009253f + 0.6321s - 0.7748z \end{aligned} \tag{9}$$

$$\begin{aligned} \phi_1^{a\prime} &= 0.4427h + 0.5170s + 0.4488z \\ \phi_2^{a\prime} &= 0.6249s - 0.7808z \end{aligned} \tag{10}$$

These sets show more clearly the distribution of electrons into lone pair and bonding molecular orbitals. The moments of electron distributions corresponding to the functions (9) and (10) are quite different from the moments obtained with the functions (5) and (6). The moments are shown in Table II. It is clear that ϕ'_2 and $\phi^{a\prime}_2$ give quite appreciable lone pair moments. Of course neither the total resultant dipole moment nor the molecular energy is changed by this orthogonal transformation.

TABLE II

DIPOLE MOMENTS (IN DEBYE UNITS)

Moments ($-2\, ea_0 \int \phi_i\, z\, \phi_i\, dv$)

($z = r_F \cos \theta_F$; θ_F = angle between electron distance from F atom and internuclear axis)

Function	Exact value	Approximate value
ϕ_1	−2.7198	−2.8426
ϕ_2	+0.9645	+0.9660
ϕ_3	−0.0015	Zero
$ea_0 Z_H r(F - H)$	+4.4042	+4.4042
M (total)	+2.6474	+2.5276
Moments from transformed functions (9), (10)		
ϕ_1'	−4.5484	−4.6526
ϕ_2'	+2.7830	+2.7758
$\phi_3' = \phi_3$	−0.0015	Zero
$ea_0 Z_H r(F - H)$	+4.4042	+4.4042
M (total)	+2.6473	+2.5274

An equivalent orbital representation of the lone pair electrons can be obtained from ϕ'_2 (or $\phi^{a\prime}_2$), ϕ_4 and ϕ_5 by a further orthonormal transformation. Let χ_{l_1}, χ_{l_2}, χ_{l_3} be the equivalent orbital functions which have the forms and properties described in the first paragraph (see also reference 1 for further details). Then

$$\begin{pmatrix} \chi_{l_1} \\ \chi_{l_2} \\ \chi_{l_3} \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{3}} & \frac{\sqrt{2}}{\sqrt{3}} & 0 \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} \phi_2' \text{ or } \phi_2^{a\prime} \\ \phi_4 = x \\ \phi_5 = y \end{pmatrix} \tag{11}$$

and, for example

$$\begin{aligned} \chi_{l_1} &= -0.00534f + 0.3649s - 0.4474z + 0.8165x \\ \chi_{l_1}^a &= 0.3608s - 0.4508z + 0.8165x \end{aligned} \tag{12}$$

χ_{l_2}, etc., may be obtained also from equations (9, 10, 11). The moment of the distribution $(|\chi_{l_1}|^2 + |\chi_{l_2}|^2 + |\chi_{l_3}|^2)$ is, of course identical with the moment of the distribution $|\phi'_2|^2$. However, the forms of the equivalent functions (12) enable one to estimate roughly the angle between lone pairs, and to deduce additional features of the electron distribution. In the notation of ref. (2)

$$\chi_{l_1}^a = \cos \epsilon_1 s + \sin \epsilon_1 \cos \gamma\, z + \sin \epsilon_1 \sin \gamma\, x$$

where γ is the angle between $\chi_{l_1}^a$ and the internuclear axis. Using $\chi_{l_1}^a$ in equation (12)

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[13] E. Safari, *Ann. phys.*, Series 12, **9**, 203 (1954).

$$\sin \epsilon_1 \cos \gamma = -0.4508; \sin \epsilon_1 \sin \gamma = 0.8165$$
$$\sin \epsilon_1 = 0.93268; \sin \gamma = 0.87544; \cos \gamma -0.48334.$$

If β is the angle between lone pairs, since

$$\sin (\beta/2) = (\sqrt{3}/2) \sin \gamma$$

then $\beta = 98°36'$.

In an equivalent orbital representation, there is a single bonding function for HF, which is just ϕ'_1 (or $\phi_1{}^{a\prime}$). The approximate function may be written in the form

$$\phi_1{}^{a\prime} = \chi_B{}^a = \mu h + \lambda (\cos \epsilon_b s + \sin \epsilon_b z) \qquad (13)$$

and from (10) it is found that $\lambda = 0.68469$, $(\lambda/\mu) = 1.55$, $\cos \epsilon_b = 0.75523$ and $\sin \epsilon_b = 0.65547$. The polarity ($H^+F^-$) is much higher, as measured by (λ/μ), than the polarity of a function made to give the correct dipole moment. For example, from the previous work,[2] such a function with $\beta = 98.5°$, will have (λ/μ) about equal to 1.09.

If the angle β between lone pairs is accepted as about 98.5°, it is of interest to compute the position of the ring of maximum electron density in the lone pair region of the molecule. This calculation is interesting in connection with association of HF to form polymers. Electron diffraction experiments[14] indicate that the principal associated form has a zig-zag structure in which the average F–F–F angle is 140 ± 5°, and the H atoms are on line with the F atoms to about ±15°. It might be expected that the H atom of one molecule would attach itself at the position of maximum electron density in the lone pair region of another molecule, and that the polymer is formed by repetition of this process. The calculation of the angle $\phi_{max.}$ which the ring of maximum density makes with the bond axis was made in the former paper[2] for several values of the angle β. The requisite formulas are given in that paper and will not be repeated here. For $\beta = 98.5°$, with the values of the parameters given here from (12) and (13), it is found that $\theta_{max.}$ is about 141°.

Sources of Integrals.—All integrals over atomic orbitals may be evaluated exactly except two-center exchange integrals, and even for these, five or six terms of the infinite series are sufficient. Formulas suitable for direct numerical evaluation are available for most integrals. A large number of integrals have been evaluated and tabulated by Kotani, *et al.*,[15] but uncertainties in interpolation made recalculation preferable in the present work. These tables, however, served as a valuable check. After most of the required integrals had been calculated, the results and tables of integrals for HF of Kastler[16] became available, and provided additional checks on the integrals.

The one-centered integrals were evaluated from the formulas of Coulson,[17] Barnett and Coulson[18] and Roothaan[19]; some integrals were computed by several methods. Two-centered integrals were computed at the normal H–F distance, $1.7328a_0$.[11] Two-centered Coulomb integrals were obtained from the formulas of Roothaan.[19] All hybrid integrals were evaluated by the analytical methods of Barnett and Coulson. Two-centered exchange integrals were computed by the methods of Ruedenberg[20]; numerical integrations were used for his ϕ_{nn}-functions, while his B_j functions were interpolated from the tables of Kotani.[15] Tables of all integrals used in these calculations are available.[21]

[14] S. H. Bauer, J. Y. Beach and J. H. Simons, THIS JOURNAL, **61**, 19 (1939).

[15] M. Kotani, A. Amemiya and T. Simose, *Proc. Phys.-Math. Soc. Japan*, **20**, Extra No. 1 (1938); **22**, Extra No. 1 (1940).

[16] The integrals are tabulated in ref. 5. The author is very grateful to Dr. Kastler for furnishing him a copy of reference 5 before its publication.

[17] C. A. Coulson, *Proc. Cambridge Phil. Soc.*, **38**, 210 (1941).

[18] M. P. Barnett and C. A. Coulson, *Phil. Trans. Roy. Soc.* (*London*), **A243**, 221 (1951).

[19] C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 1445 (1951).

[20] K. Ruedenberg, *ibid.*, **19**, 1459 (1951).

[21] Tables of integrals have been deposited as Document 4451 with the ADI Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints or $1.25 for 35 mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

ROCHESTER, N. Y.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ETHYL CORPORATION]

The Compound Na_9Pb_4

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A little-known region of the Na–Pb equilibrium diagram, in the vicinity of the composition Na_9Pb_4, was reinvestigated by means of thermal and microscopic analysis. The work demonstrated the existence of a hitherto unrecognized open-maximum compound at the Na_9Pb_4 composition. The neighboring compound Na_5Pb_2 was shown to be a peritectic rather than an open-maximum compound.

Previous investigations[2] of the complicated Na–Pb equilibrium system have indicated the existence of five compounds: Na_2Pb_5, NaPb, Na_2Pb, Na_5Pb_2 and Na_4Pb. In addition, although neither compound is formed from melts, Na_4Pb_7 and Na_4Pb_9 have been reported in liquid ammonia solution.[3] The compound Na_2Pb[4] was considered to be formed at 182° by the solid–solid reaction $Na_5Pb_2(s) + NaPb(s) = 3Na_2Pb(s)$. The other compounds in the phase diagram were reported to be of the open-maximum type, with Na_5Pb_2 giving the highest

[1] (a) The Haloid Corporation, Rochester, N. Y. (b) Mine Safety Appliances Co., Pittsburgh 8, Pa.

[2] M. Hansen, "Der Aufbau Zweistofflegierungen," Julius Springer, Berlin, 1936.

[3] E. Zintl, J. Goubeau and W. Dullenkopf, *Z. physik. Chem.*, **A154**, 37 (1931).

[4] G. Calingaert and W. J. Boesch, THIS JOURNAL, **45**, 1901 (1923)