212. *Some Considerations on the Strengths of Hybrid Bonds in Excited States of the Hydrogen Molecule-ion.*

By H. O. PRITCHARD and H. A. SKINNER.

The potential-energy curves for a series of defined states of H_2^+ are calculated by the molecular-orbital method. The results are compared with those of a similar study by Pauling and Sherman, from which the present work differs in that the correct H atom eigenfunctions are used in place of the approximate Slater eigenfunctions.

The calculated ratio of 1 : 3 : 4 obtained by Pauling and Sherman for the relative strengths of *s–s*, *p–p* and sp^3–sp^3 bonds in the 2- and 3-quantum states of H_2^+ is not found from the results of this paper.

Calculations on the ground state of H_2^+ show that the description of this state as a 1*s*–2*p* hybrid ($Z = 1$) gives a very close approximation in respect of the energy, but the calculated bond length is too small, and the calculated force constant too large. The additional variation in Z (Dickinson) corrects the error in r_e.

An examination of Badger's rule ($k_e^{-\frac{1}{3}} \propto r_e$) applied to the calculated constants for the different states of H_2^+ shows that the rule is followed rather closely when states of similar bonding are considered as a class.

AN important postulate of the quantum-mechanical theory of directed valence, as developed in a simple way by Slater (*Phys. Review*, 1931, **38**, 1109) and Pauling (*J. Amer. Chem. Soc.*, 1931, **53**, 1367), is that the relative "bond-forming power" of an orbital is proportional to the magnitude of the angular part of the orbital along the bond axis. According to this postulate, the "bond-forming powers" of *s*-, *p*-, and sp^3-orbitals of a given atom stand in the ratio $1 : \sqrt{3} : 2$, corresponding to a 1 : 3 : 4 ratio between the strengths of *s–s*, *p–p*, and sp^3–sp^3 bonds formed by the atom. In their paper "A Quantitative Discussion of Bond Orbitals," Pauling and Sherman (*J. Amer. Chem. Soc.*, 1937, **59**, 1450) sought to verify this simple postulate by a calculation (using the method of molecular orbitals) of the strengths of the 1-electron bond in various hypothetical states of the H_2^+ molecule-ion. They obtained the ratio 1 : 2·7 : 4·1 for the order of the strengths of the 2-quantum *s–s*, *p–p*, and sp^3–sp^3 bonds in H_2^+, in good agreement with the expected 1 : 3 : 4 ratio.

The quantitative treatment of hybridization by Pauling and Sherman makes several simplifying assumptions. For reasons explained in their paper, Pauling and Sherman chose to use the approximate Slater wave-functions in constructing molecular orbitals describing excited states of the H_2^+ molecule-ion. The use of these approximate atomic orbitals required other, and more drastic, approximations in the subsequent evaluation of the energy integrals.

We have thought it of interest to re-examine the problem, following essentially the procedure of Pauling and Sherman, except that we use the correct H atom eigenfunctions throughout, and thus avoid all approximations except the general one of the L.C.A.O. method, *i.e.*, the approximation involved in representing the molecular orbitals by some linear combination of atomic orbitals.

Excited States of H_2^+: *2-Quantum States.*—We consider the 1-electron bonding in various hypothetical states of H_2^+, presumed to be derived from a proton and an *excited* H atom. Representing the molecular orbitals by

$$\psi = c(\phi_A + \phi_B) \qquad (1)$$

where ϕ_A and ϕ_B are similar atomic orbitals for the atoms A and B, the case of 2*s*–2*s* bonding requires that ϕ_A and ϕ_B be 2*s* atomic orbitals, and the case of 2*p*–2*p* bonding correspondingly that ϕ_A and ϕ_B are $2p_z$ orbitals. The 2*s*, $2p_z$ orbitals are known precisely for the H atom, *viz.* :

$$\phi_A^s = \sqrt{\frac{\beta^3}{\pi}} \cdot (1 - \beta r_A)e^{-\beta r_A} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$\phi_A^p = \sqrt{\frac{\beta^5}{\pi}} \cdot r_A \cos\theta_A \, e^{-\beta r_A} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$\beta = Z/2a_0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

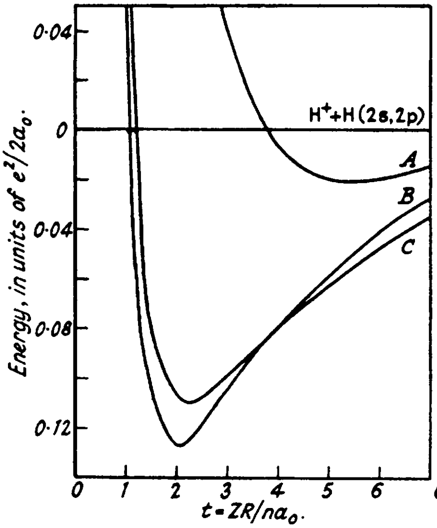
The potential-energy curves ($Z = 1$) calculated for *s*–*s* and *p*–*p* bonding with equations (1), (2), and (3) are shown by curves *A* and *B* of Fig. 1. Curve *C* of the same figure represents the most stable *hybrid* arising from the interaction of states A and B. The eigenfunction ψ_h representative of the hybrid state C is given by :

$$\psi_h = a\psi_I + b\psi_{II} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

where ψ_I describes state A, and ψ_{II} describes state B. Curve *C* corresponds to values of the mixing coefficients *a*, *b* in equation (5) which minimize the energy integral $\int\psi_h H\psi_h d\tau$ at each value of the internuclear separation.

FIG. 1.

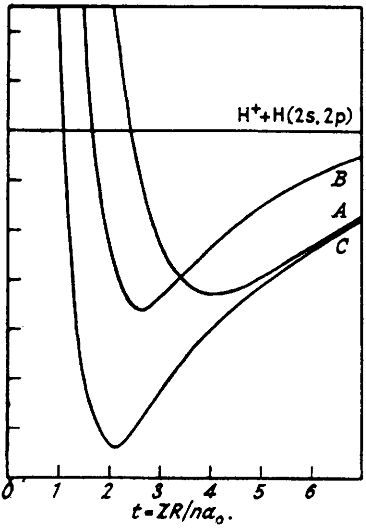
2-Quantum States of H_2^+.



A, 2s–2s. *B*, 2p–2p. *C*, *Best* sp-*hybrid*.

FIG. 2.

2-Quantum States of H_2^+.



A, *B*, sp³-*Hybrids*. *C*, *Best* sp-*hybrid*.

There are both qualitative and quantitative differences between the curves in Fig. 1 and the corresponding curves calculated by Pauling and Sherman. The numerical differences—expressed in terms of the calculated dissociation energies D_e, and equilibrium distances r_e—are summarized in Table I. The D_e values are measured in units $e^2/2a_0$ ($e^2/2a_0$ = ionization potential of normal H atom), and the r_e values are in atomic units (*i.e.*, units of a_0 = Bohr radius = 0·529 A.).

TABLE I.

Calculated constants in excited states of H_2^+.

Bond.	D_e (this paper).	r_e.	D_e (P. and S.).	r_e.
2*s*–2*s*	0·0207	10·72	0·040	7·8
2*p*–2*p*	0·1094	4·58	0·108	4·6
Best *s*–*p* hybrid	0·1272	4·10	0·170	4·72

The qualitative differences between the curves in Fig. 1 and the Pauling–Slater curves are most apparent in case of curve *C* and its counterpart. The differences originate in the nodeless character of the Slater 2*s* atomic orbital, compared with the nodal function (equation 2). Thus the Pauling–Sherman analogue of curve C corresponds at all distances to positive values for the ratio a/b of the mixing coefficients a, b of equation (5), whereas curve C reflects a reversal in sign of a/b in the region $t = 3{\cdot}7$ ($t = Z\mathbf{R}/na_0$).

The point is perhaps emphasized more clearly by Fig. 2. In this we have plotted energy for the sp^3-bonded H_2^+ molecule. These are the states described by the molecular orbital

$$\psi_{sp^3} = c(\phi_A^{sp^3} + \phi_B^{sp^3}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $\phi_A^{sp^3}$ is a hybrid atomic orbital,

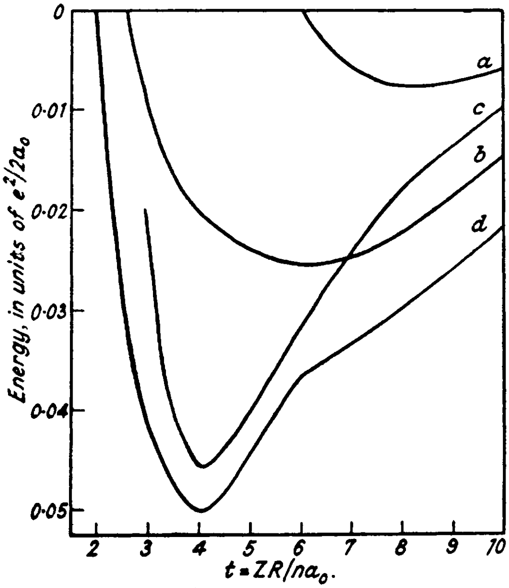
$$\phi_A^{sp^3} = \tfrac{1}{2}\phi_A^s \pm \frac{\sqrt{3}}{2}\phi_A^p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Curve A results from use of the positive sign in (7), and curve B from that of the negative sign. Curve C, representing the best s–p admixture, is the same as curve C of Fig. 1.

Pauling and Sherman, using Slater $2s$ functions for ϕ_A^s, ϕ_B^s found that the sp^3-hybrid (positive sign) closely approximates the best bonding attainable from s–p mixing. This is not the case when the true ϕ_A^s, ϕ_B^s are used, for neither of the curves A and B of Fig. 2 corresponds to binding of comparable firmness to that shown in curve C; only at large internuclear separations does curve A begin to resemble curve C.

FIG. 3.

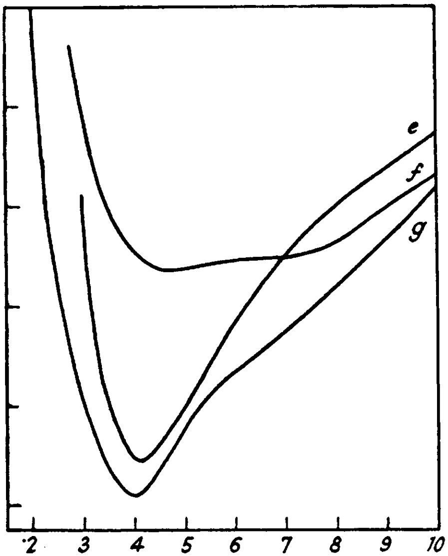
3-*Quantum States of* H_2^+ [H^+ + H (3s, 3p, 3d)].



a, 3s–3s. *b*, 3p–3p. *c*, 3d–3d. *d*, *Best* spd-*hybrid*.

FIG. 4.

3-*Quantum States of* H_2^+ [H^+ + H (3s, 3p, 3d)].



e, sd-*Hybrid*. *f*, sp-*Hybrid*. *g*, pd-*Hybrid*.

Excited States of H_2^+: 3-*Quantum States*.—In this section, the calculations are extended to the 3-quantum states of H_2^+, covering the bonding types s–s, p–p, d–d, and the hybrid admixtures sp-, sd-, pd-, and spd-. The eigenfunctions of the 3-quantum states of the H atom were used in the following form :

$$\phi_A^{3s} = \sqrt{\frac{\gamma^3}{\pi}}\cdot(1 - 2\gamma r_A + \tfrac{2}{3}\gamma^2 {r_A}^2)e^{-\gamma r_A} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$\phi_A^{3p_z} = \sqrt{\frac{2\gamma^5}{3\pi}}\cdot r_A(2 - \gamma r_A)\cos\theta_A e^{-\gamma r_A} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$\phi_A^{3d_z} = \sqrt{\frac{\gamma^7}{2\pi}}\cdot {r_A}^2(\cos^2\theta_A - \tfrac{1}{3})e^{-\gamma r_A} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$\gamma = Z/3a_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The calculated potential-energy curves ($Z = 1$) for the s–s, p–p, and d–d bonded states are shown in curves a, b, and c of Fig. 3. The curve d in this same figure represents the best bonding attainable by *spd*-hybridization. The molecular constants of these states are summarized in Table II, and compared with the values calculated by Pauling and Sherman on the basis of the Slater approximations to equations (8), (9), and (10).

Curves representing the best hybrid states attainable from *sp*-, *sd*-, and *pd*-mixing are shown separately in Fig. 4.

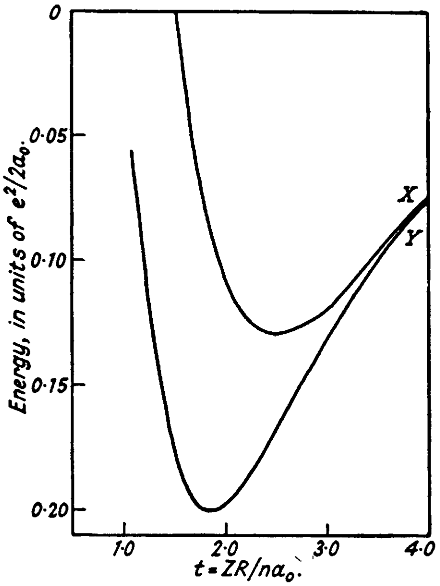
TABLE II.

Calculated constants in 3-quantum states of H_2^+.

Bonding.	D_e (this paper).	r_e	D_e (P. and S.).	r_e
3*s*–3*s*	0·00765	24·73	0·028	16·0
3*p*-3*p*	0·0254	18·52	0·074	10·5
3*d*–3*d*	0·0453	12·22	—	—
sp-Hybrid	0·0264	14·33	0·12	11·0
sd-Hybrid	0·0453	12·22	—	—
pd-Hybrid	0·0490	11·82	—	—
spd-Hybrid	0·0501	11·92	—	—

The Ground-state of H_2^+: 1s-2p *Hybridization.*—It is well known that the binding in the ground state of the H_2^+ ion is not adequately described in terms of 1*s*–1*s* bonding. The potential-energy curve for the 1*s*–1*s* type of bonding ($Z = 1$) is shown in curve *X* of Fig. 5, and represents a form of bonding appreciably weaker than exists in the actual molecule. Curve *X* shows a dissociation energy only 63% of the experimental value. The calculated dissociation energy can be raised to 80% of the true value by varying the parameter *Z* (Finkelstein and Horwiotz, *Z. Physik*, 1928, **48**, 118) and raised still further to 97%, by simultaneously varying *Z* and using hybrid 1*s*–2*p* orbitals (Dickinson, *J. Chem. Phys.*, 1933, **1**, 317). The curve *Y* of Fig. 5 is calculated for the best 1*s*–2*p* hybrid, without, however, making any variation in *Z* from the value $Z = 1$. It leads to a dissociation energy almost equal to that obtained by Dickinson.

FIG. 5.



$H^+ + H(1s)$. *X*, 1s–1s. *Y* = 1s–2p-*Hybrid*.

These calculations suggest that the most effective *single* addition to the 1*s*–1*s* description of the bonding in the ground state of H_2^+ is attained by the hybridization of the 1*s* with the $2p_z$ atomic orbitals, although there is a very large energy separation (10·2 ev.) between these orbitals.

In case of the ground state of the H_2 molecule, the calculations of Rosen (*Phys. Review*, 1931, **38**, 2099) show that a mixing of 1*s* and $2p_z$ orbitals leads to a significant increase in the calculated energy, but here variation in the parameter *Z* is more effective *per se* than is the polarization of the 1*s*-orbitals. By simultaneous variation in *Z*, and mixing of 1*s*–$2p_z$ orbitals, Rosen arrived at a dissociation energy approaching 85% of the experimental value. It is interesting, however, that, at internuclear separations comparable with those near the equilibrium separation in H_2^+, Rosen finds that the effect of hybridization asserts itself as the dominant factor in raising the energy relative to that of the 1*s*–1*s* bonded molecule.

The very significant contribution of the $2p_z$ orbitals to the bonding in H_2^+, and the lesser but nevertheless important contribution in H_2, should be stressed. The relatively large energy separation of the 1*s* and 2*p* atomic orbitals of the H atom is seen to present a barrier insufficient to prevent an appreciable mixing of these orbitals when bond formation occurs. As a consequence, it is reasonable to expect that hybridization occurs more frequently than not, for in general the energy separations between neighbouring orbitals in atoms other than hydrogen are not larger than in the H atom itself.

DISCUSSION.

From the data listed in Table I and II, it is apparent that use of Slater functions to describe excited states of H_2^+ (coupled with the approximations attached thereto) leads to results markedly different quantitatively from those of this paper. For example, if we confine attention to the *relative* strengths of different bond types, we find quite different ratios from those of Pauling and Sherman, *viz.* :

(a) 2-*Quantum states*, *ss* : *pp* : best *sp*-hybrid = 1 : 5·3 : 6·2, compared with 1 : 2·7 : 4·1 (Pauling).

(b) 3-*Quantum states*, *ss* : *pp* : best *sp*-hybrid = $1 : 3{\cdot}3_5 : 3{\cdot}5$, compared with $1 : 2{\cdot}6_4 : 4{\cdot}0_7$ (Pauling).

The differences in these ratios are more serious than in a purely quantitative sense, for, whereas Pauling and Sherman found an approximate *constancy* in the ratios of *ss* : *pp* : sp^3-hybrid in passing from the 2- to the 3-quantum states, our ratios do not show this type of behaviour. We hesitate to conclude that, in the general case, the strength of a hybrid bond stands neither in a simple nor in a constant ratio to the strengths of its parent bonds; but, on the other hand, it seems to us that the assumption of a simple 1 : 3 : 4 ratio for the ratio *ss* : *pp* : sp^3–sp^3 bond strengths has little real justification.

A further point of departure from Pauling and Sherman is seen in the comparison of the calculated bond lengths (r_e). The calculations of this paper show that the hybrid bonds are both stronger and shorter than their parents—*e.g.*, in the 2-quantum states r_e of the best hybrid is noticeably shorter than r_e of the *s*–*s* or *p*–*p* bonded states. Pauling and Sherman, on the contrary, found the r_e of the hybrids to lie in between the r_e of the parent bonds. Indeed, Pauling and Sherman concluded in their paper that "there is no simple inter-relation between bond-energy and internuclear distance." The calculations of this paper, whilst showing no very sharp dependence of dissociation energy on bond length, reveal that there exists a rough relationship in the sense that the shorter the bond, the stronger it is.

There are some interesting relations between the calculated r_e values and the force constants (k_e) of the various states of the H_2^+ molecule-ion. The k_e values were obtained by fitting Morse curves through three points calculated in the vicinity of the equilibrium position, as described by Rosen (*loc. cit.*) and Coulson (*Trans. Faraday Soc.*, 1937, **33**, 1485). These are given in Table III, together with the calculated r_e and D_e, expressed now in the more conventional units of A. and electron-volts.

TABLE III.

Calculated constants of H_2^+.

Bond.	r_e (A.).	D_e (ev.).	k_e (dynes × 10^5/cm.).	Bond.	r_e (A.).	D_e (ev.).	k_e (dynes × 10^5/cm.).
1*ss*	1·318	1·755	0·979	1*s*2*p*	0·979	2·706	2·152
2*ss*	5·67	0·2797	0·0172	2*s*2*p*	2·170	1·721	0·208
3*ss*	13·09	0·1035	0·00148	3*s*3*p*	7·583	0·358	0·0040
2*pp*	2·42	1·480	0·0943	3*p*3*d*	6·255	0·663	0·0197
3*pp*	9·80	0·343	0·00168	3*s*3*p*3*d* ...	6·308	0·678	0·0161
3*dd*	6·467	0·613	0·0205	${}^2\Sigma^+{}_{g\ (\mathrm{obs.})}$	1·06	2·77	1·566

The relation of k_e to r_e is shown in the plot of $k^{-\frac{1}{3}}$ against r_e (Badger's rule) in Fig. 6. The straight lines in Fig. 6 are drawn through points corresponding to bonds of similar description—*e.g.*, curve *A* covers the 1*ss*-, 2*ss*-, and 3*ss*-bonded states. Whilst it is perhaps incautious to draw conclusions from our limited data, Fig. 6 gives some ground for examining the Badger rule in series of similarly-bonded molecules—*e.g.*, the series of alkali-metal hydrides. This point is taken up more fully in the Appendix.

The present work was undertaken with the purpose of establishing more firmly Pauling and Sherman's semi-empirical relation between the strengths of hybrid and parent bonds. In this respect, the results obtained are disappointing, in that they suggest that hybrid bonding requires individual treatment in each specific case, and that simple generalizations are at best approximations. Some useful features that emerge from the present work may have a wider significance than in the particular and exceptional case of the H_2^+ molecule. For example, the considerable effect arising from the interaction of the states 1*ss* and 2*pp* in H_2^+ suggests that the simple description of many chemical bonds in terms of a single bond type—*e.g.*, *s*–*s*-, *p*–*p*-, *s*–*p*-bonds—may require revision in terms of hybrid descriptions. Recent experimental evidence (Townes and Dailey, *J. Chem. Physics*, 1949, **17**, 782) and some theoretical considerations by Moffitt (*Proc. Roy. Soc.*, 1950, *A*, **202**, 534) point in the same direction.

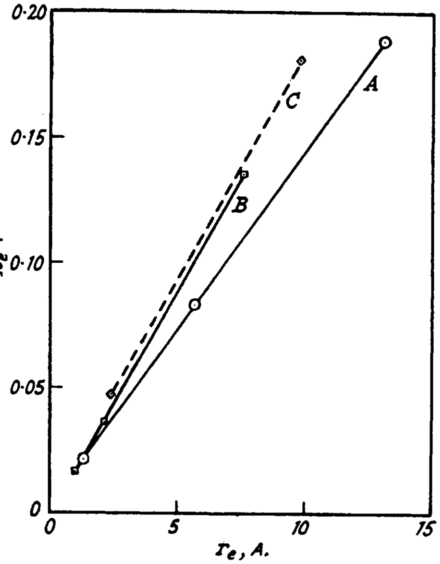
APPENDIX.

The empirical relation between force constant (k_e) and equilibrium bond length noticed by Badger (*J. Chem. Physics*, 1934, **2**, 128) is expressed by the equation :

$$k_e\,(r_e - d_{ij})^3 = C_{ij} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (i)$$

FIG. 6.

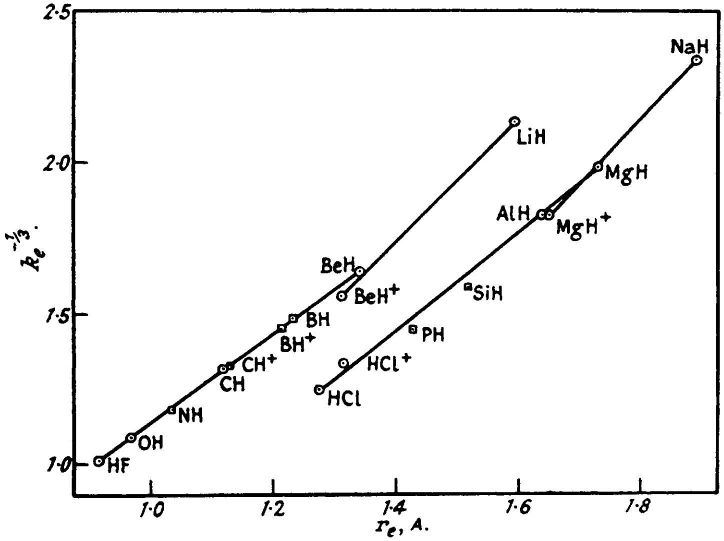
Badger's rule. Plot of $k_e^{-\frac{1}{3}}$ *against* r_e.



A, ss-*Bonds*. *B*, sp-*Hybrid bonds*. *C*, pp-*Bonds*.

FIG. 7.

Badger's rule for hydrides of 1*st and* 2*nd period.*



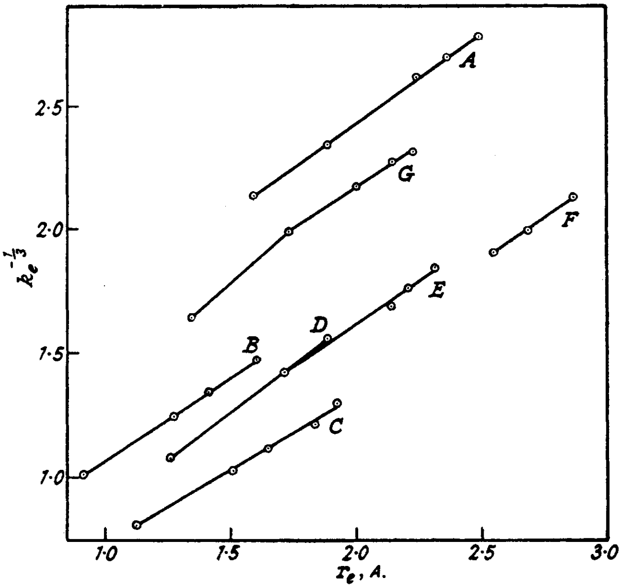
○ *Well-established experimental data.*

⊡ *Less-well-established experimental data.*

where d_{ij}, C_{ij} are constants characteristic of diatomic molecules made up from one element in the i-th row and one in the j-th row of the periodic table. In favourable cases—as, *e.g.*, in the ground states of the hydrides of the 1st- and 2nd-row elements (Fig. 7)—the Badger rule holds good with an accuracy of the order 1%. In Fig. 7, separate lines have been drawn through the points HF $\longrightarrow$ BeH, and BeH$^+$ $\longrightarrow$ LiH (row 1), and similarly for the points HCl $\longrightarrow$ MgH, MgH$^+$ $\longrightarrow$ NaH (row 2), in order to discriminate between bonding which in first-order approximation may be described as *p–s* (HF $\longrightarrow$ BeH; HCl $\longrightarrow$ MgH), or as *s–s* (BeH$^+$ $\longrightarrow$ LiH; MgH$^+$ $\longrightarrow$ NaH).

FIG. 8.

Badger's rule applied to families.

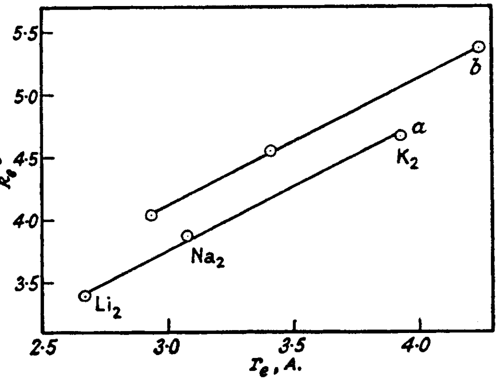


A, LiH, NaH, KH, RbH, CsH.
B, HF, HCl, HBr, HI.
C, CO, SiO, GeO, SnO, PbO.
D, BF, BCl, BBr.
E, BCl, AlCl, GaCl, InCl.
F, TlCl, TlBr, TlI.
G, BeH, MgH, CaH, SrH, BaH.

It is not our purpose to examine Badger's rule in the form in which it was originally proposed, but rather to apply it to series of similarly-bonded molecules. Such a series is provided by the alkali-metal hydrides LiH, NaH, KH, RbH, CsH, in which the variation is in the principal quantum number of the valence electrons, comparing in this sense with the variation in passing from the 1*ss* $\longrightarrow$ 2*ss* $\longrightarrow$ 3*ss* states of H_2^+. Fig. 8 shows some examples of this mode of

FIG. 9.

Badger's rule for $^1\Sigma_g^+$ *and* $^1\Pi_u$ *states of* Li_2, Na_2, *and* K_2.



a, $^1\Sigma_g^+$ *States.* *b*, $^1\Pi_u$ *States.*

application of Badger's rule. The examples shown do not exhaust the possibilities of the method, and several other families not shown give good linear plots—*e.g.*, [O_2, SO, S_2, Se_2, Te_2]; [CS, SiS, PbS]; [Cl_2, Br_2, I_2]; [P_2, PN, N_2].

Some significant deviations from linearity in a series may be caused by abrupt changes in bond character along a given series. For example, although the alkali-metal hydrides form a good linear family (curve *A*), the sub-group B hydrides (CuH, AgH, AuH) give a scattered set of points lying well removed from curve *A*. We think it possible that the difference between the A and the B sub-groups arises from the low-lying ^2D states of B sub-group metals (^2D in Cu; $3d^9$, $4s^2$) giving weight to a measure of *d*-orbital bonding in the case of CuH, AgH, and AuH. Similarly, the break in the curve *G* (BeH, MgH—CaH, SrH, BaH) may reflect the onset of some degree of *d*-bonding at CaH—since the atoms Ca, Sr, Ba, possess relatively low-lying ^3D states.

Although the halogens Cl_2, Br_2, I_2, ICl, ClBr, form a good example of a linear family, F_2 and F-containing interhalogens (FCl, FBr) lie off the main line. We can advance no good reason at the present for this deviation from linearity on the part of F-containing halogen compounds, but it may be significant in this respect that the dissociation energy of F_2 is low (Evans, Warhurst, and Whittle, *J.*, 1950, 1524) by comparison with an extrapolation based on the dissociation energies observed for Cl_2, Br_2, and I_2.

A neat illustration of the point that in making a Badger's rule plot for a family of compounds, the family should be restricted—in the sense that the bond character remains similar along the family series, or, alternatively, suffers no abrupt change—is provided by Fig. 9. This shows the plot for Li_2, Na_2, and K_2 in (*a*) the ground ($^1\Sigma_g^+$) states, and (*b*) the excited ($^1\Pi_u$) states. We note that identical states give good linearity, but the two sets of data are separate and require two lines for their description.

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CHEMISTRY DEPARTMENT, UNIVERSITY OF MANCHESTER. [*Received, December 8th*, 1950.]