proaches zero as the $2r$ decreases to a certain value. In the O—H···O bond, the smallest distance between two oxygens at which the O—H distance has been measured is 2.478 A in KH_2PO_4, and even in this length of r, d is 0.154 A.[1] On the other hand, in the F—H···F bond, it was reported that, at the value of $2r=2.26$ A in KHF_2, d is at least less than ± 0.06 A and the bond has a symmetrical configuration.[2,3] In NH_4HF_2, the F—F distance is 2.36 A,[4] and it is interesting to know where the hydrogen is lying between two fluorines.

We have measured the lines of H^1 and F^{19} nuclear resonances in powdered state at room temperature. The photograph of the fluorine resonance is shown in Fig. 1. By taking the average over ten experimental lines, we obtained the value of the second moment, $(\Delta H_2{}^2)=68.7\pm 3.5$ gauss^2 for F resonance and $(\Delta H_2{}^2)=22.7\pm 3.5$ gauss^2 for H resonance. The theoretical second moment except the intramolecular part in an FHF ion can be calculated by using the structure determined by x-ray.[4] For F resonance the main part of the second moment arises from this intra-FHF part, which amounts to be 57.8 gauss^2 for a symmetrical configuration of the molecule with the proton at rest.

We have considered the following two cases: first, the proton is lying in the potential having one minimum; second, it is lying in the potential having two minima. In the first case, vibrational motion of the proton along the bond affects the second moment, if the frequency of the vibration is higher than that of the spin-spin interactions. If we assume that the vibration is a harmonic oscillator and use the result of infrared absorption, $\nu(\text{F—H})=2000$ cm^{-1}, then the amplitude of the oscillator becomes 0.13 A for the symmetrical F—H—F molecule. The experimental second moment gives the amplitude of 0.11 A for the most probable value. In the second case, to check the possibility for determining the separation of the two minima of the potential when the proton is in the tunneling motion, we have calculated the second moment for the model as shown in Fig. 2. By taking V_0 as a parameter, the experimental second moment determined the value of d. We obtained $d=0.074$ A for the most probable value and $d=0.11$ A for the largest value of the experimental error.

K. Nakamoto, M. Margoshes, and R. E. Rundle plotted the O—H distances against O—O distances in the O—H···O bond. These distances were measured by neutron diffraction or NMR method.[5] If we assume that this relation between r and d in the O—H···O bond can be applied to the F—H···F bond by using the ionic radius of F in place of O, the deviation parameter d will be about 0.13 A for the FHF in NH_4HF_2. However, this deviation is slightly larger than our experimental results for the model of the double minima potential. Therefore, it may be accepted that F—H···F bond has a stronger tendency to form a symmetrical configuration than the O—H···O bond. This fact may be caused by the larger electronegativity of fluorine, and it is suggested that the electrostatic interaction plays an important role for the formation of a symmetrical bond.

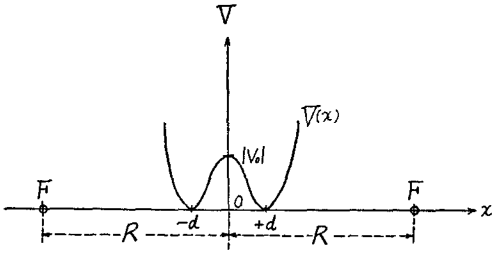

FIG. 2. The potential function having two minima used for the calculation of the second moment of the FHF ion.

$$V(x)=|V_0|+kx^2+[k^2/(4|V_0|)]x^4.$$

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[1] G. E. Bacon and R. S. Pease, Proc. Roy. Soc. (London) **A220**, 397 (1953); Peterson, Levy, and Simmonsen, J. Chem. Phys. **21**, 2084 (1953).

[2] Waugh, Humpherey, and Yost, J. Phys. Chem. **57**, 486 (1953).

[3] E. F. Westrum, Jr., and K. S. Pitzer, J. Am. Chem. Soc. **71**, 1940 (1949).

[4] M. T. Rogers and L. A. Helmholz, J. Am. Chem. Soc. **62**, 1533 (1940); R. W. G. Wyckoff, *Crystal Structures*, Interscience Publishers, Inc., (New York, 1948), Sec. I.

[5] Nakamoto, Margoshes, and Rundle, J. Am. Chem. Soc. **77**, 6480 (1955).

Spectrophotometric Determination of the Electron Affinity of Fluorine

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ULTRAVIOLET spectroscopy of ionic solutions may be used as an important source of thermochemical data. The purpose of this note is to present a calculation of the electron affinity of fluorine based on such spectroscopic data. A direct determination of E_F might have been based on the investigation of the absorption spectrum of the fluoride anion in aqueous solution, and by using the well-known empirical correlation between the energy of the electronic transition and the sum of the electron affinity and the solvation energy for the anion.[1] This band has not been investigated as it is masked by the absorption of the solvent. However, this difficulty can be overcome by using an "electron acceptor" which binds the electron in the excited state more strongly than in the former case.

Inspection of the data concerning the electron transfer spectra of a particular cation with various anions indicates a shift of the charge transfer spectra of the anions to longer wavelengths. This method employing the data for the ferric ion pairs was suggested by Evans *et al.*,[2] but the data for the ionic solvation ener-

TABLE I. Thermochemical and spectrophotometric data for ferric-ion pairs.[a]

Anion	$S_X^- + E_X$[b]	S_X[c]	$h\nu_{max}$[d,e]	$-\Delta H_f$[e]	$I-\chi$
Cl^-	176	2.5	91.5	−8.5	74.5
Br^-	163	3.5	76	−6.1	77
OH^-	172	6.5	90	1.2	75
F^-		2	120	−7.5	(75)

[a] All energetic data presented in kcal/mole.

[b] S_X^- from references 1, 3, 4; E_X from reference 7.

[c] Reference 1(b).

[d] Reference 1(a).

[e] M. G. Evans and N. Uri, Symposia Soc. Exptl. Biol., No. 5, 130 (1951).

gies used by them are not consistent with the accepted values[3,4] and their treatment did not take account of all the necessary energetic terms.

The following cycle was used for the evaluation of the energy of the electronic transition

$$\begin{tikzcd}
Fe_{aq}^{+3}+X_{aq}^- \arrow[r, "E_X+S_X^- - I"] & Fe_{aq}^{+2}+X_g \arrow[d, "-S_X+\chi"] \\
(Fe^{+3}X^-) \arrow[u, "-\Delta H_f"] \arrow[r, "h\nu"] & (Fe^{+2}X),
\end{tikzcd}$$

where I represents the ionization energy of the ferrous ion in solution, χ is the enthalpy change for the formation of the Franck-Condon excited state from Fe_{aq}^{+2} and X_{aq} in their equilibrium states, S_X^- and S_X are the solvation energies of the anion and the radical, respectively (defined as the ΔH° of the reaction $X_{aq}^- \rightarrow X_q^-$), E_X is the electron affinity of the radical, and ( ) represents the equilibrium structure of the hydration layer surrounding the ion pair in the ground state.

Hence we obtain

$$h\nu_{max} = E_X + S_{X^-} - \Delta H_f - S_X - I + \chi. \qquad (1)$$

By employing Eq. (1) the values of $I-\chi$ were calculated from the available data. These results are presented in Table I.

It appears that χ is approximately independent of the anion. The term χ accounts for two kinds of Franck-Condon strain: packing strain of the radical X which is relevant in the case of a polyatomic radical; and orientation strain of the solvent structure in the vicinity of the ion pair. In the case of the electron transfer spectra of anions χ is approximately constant.[1(b)] In ferric-ion pairs χ is due partly to the ferric component, so that the dependence of χ on the anion will be even smaller, and $(I-\chi)$ for F^- will be similar to the other halides. Thus we get $I-\chi = 75\pm2$ kcal. By inserting this result into Eq. (1) and by using the available data for the fluoride anion (Table I) and $S_{F^-} = 122$ kcal[3,4], we obtain $E_F = 82\pm2$ kcal. By using the relation between the electron affinity of fluorine atom and the dissociation energy of the fluorine molecule obtained from the Born-Haber cycle $E_F - 1/2 D_{F_2} = 63$ kcal, we get $D_{F_2} = 38\pm4$ kcal. These results which we based on an independent method confirm the results of recent investigations,[5,6] and agree with the value suggested by Pritchard.[7]

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[1] (a) E. Rabinowitch, Revs. Modern Phys. **14**, 112 (1942); (b) G. Stein and A. Treinin (to be published).

[2] Evans, Hush, and Uri, Quart. Rev. **6**, 186 (1952).

[3] Latimer, Pitzer, Slansky, J. Chem. Phys. **7**, 108 (1939).

[4] E. J. W. Verwey, Rec. trav. chim. **61**, 127 (1942).

[5] A. L. G. Rees, J. Chem. Phys. **26**, 1567 (1957).

[6] T. L. Bailey, J. Chem. Phys. **28**, 892 (1958).

[7] H. O. Pritchard, Chem. Rev. **52**, 529 (1953).

Evaporation of Aluminum Oxide

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BREWER and Searcy[1] have reported the vaporization rate of aluminum oxide based on the effusion rate from a tungsten cell. They assumed that a minor fraction of the effusate resulted from the reaction bebetween tungsten and aluminum oxide. It was later shown[2] that such a reaction contributes significantly to the measured effusion rates. It is the purpose of the present letter to present some evidence on the evaporation rate of alumina out of contact with a crucible.

Recently Navias[3] has made studies of the chemical stability of certain electronic tube structures which studies are pertinent to the volatility of aluminum oxide. From his data an upper limit for the evaporation rate of aluminum oxide out of contact of possible reactants has been estimated. The evaporation rate is about four thousand times less at 1900°C than the extrapolated value from Brewer and Searcy's[1] data.

Experimental résumé.—A tungsten or a tantalum tube 3 in. in length and 0.125-in. i.d. was used as a furnace. The furnace tube was surrounded by a 0.500-in. diam helix of tungsten wire. The helix served as an electron source for bombardment heating and temperatures up to 1975°C could be attained. The temperature was measured with an optical pyrometer through a hole ~0.017 in. in diameter in the furnace wall and in the center of the tube length. The apparent tube temperature was uniform along the tube length.

A 2-in. length of sapphire rod 0.030 in. or 0.050 in. in diameter was inserted axially into the upper end of the furnace so that approximately 1.3 in. of the rod was inside the furnace cavity. The sapphire rod was bound by tungsten wire to a cool region of the tungsten support rod for the furnace cylinder. Thus no portion of the hot sapphire was in contact with a solid reductant. A shield was placed so as to avoid direct