$$E = W - \frac{1}{2}(A - U), \quad (8)$$

where W is the evaporation energy for naphthalene. From the known value $W = 18.2$ k.cal.⁴, and those obtained by Clancey for E , one obtains values for $(A - U)/2$ going from 5 to 2 k.cal., which are of the order one would expect. The corresponding values of x_s at room temperature, from (7), range from 10^{-4} to 10^{-6} cm., again as we should expect. It should also be noticed that the factor outside the exponential in (6) will be essentially determined by that corresponding to p , and therefore will be practically independent of the substrate, as is observed by Clancey.

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Dipole Moment and Ionic Character

ONE well-known application of the concept of ionic-covalent resonance is in the field of dipole moments, where it has been used, in a simple way, to correlate the observed dipole moments of bonds with differences in electronegativity¹. However, recent work, notably that of Mulliken², Coulson³, and Robinson⁴, has cast doubt upon the validity of some of the assumptions made in this treatment⁵. One of these assumptions is that the dipole moment of a pure covalent bond is approximately zero.

Robinson⁴ has calculated the dipole moment, $\mu_{\text{cov.}}$, of a pure covalent HCl bond using a Heitler-London type of wave function. He obtained a value of $-0.98 D$, that is, the hydrogen atom negative, whereas the experimental value is $+1.10 D$ ⁶. He found that the calculated value of $\mu_{\text{cov.}}$ was extremely sensitive to sp hybridization of the chlorine orbital. A value of $\mu_{\text{cov.}} = +1.10 D$ is obtained with about

10 per cent s character. Robinson, therefore, points out that the observed dipole moment can be accounted for without invoking contributions by ionic structures, and concludes that "Dipole moments do not give a good method for determining the ionic character of bonds".

We have carried out the same type of calculation for hydrogen fluoride, using Robinson's equations⁴ and evaluating the appropriate integrals. Using a $2p$ fluorine orbital (unhybridized), the following values for the dipole moment of a pure covalent HF bond were obtained: (a) $\mu_{\text{cov.}} = -0.40 D$, with hydrogen-like functions and an effective nuclear charge of 4.84 for fluorine⁷, and (b) $\mu_{\text{cov.}} = -0.32 D$ using Slater functions. These values are not far from zero, and are much smaller in magnitude than the observed value of $+1.91 D$ ⁸.

Using hybridized orbitals with hydrogen-like wave-functions, the variation of $\mu_{\text{cov.}}$ with percentage s character has been calculated and is shown in the accompanying diagram. While the curve shows the same general features as that obtained by Robinson for hydrogen chloride, there is a striking difference in that $\mu_{\text{exp.}}$ for hydrogen fluoride is larger than the maximum value of $\mu_{\text{cov.}}$, namely, $+1.75 D$, corresponding to 60 per cent s character. Thus the observed dipole moment cannot be explained solely in terms of hybridization. In this case, at least, it appears that ionic terms must be added to the wave function. Another point of interest is that, for both hydrogen fluoride and hydrogen chloride, approximately the same, small, amount of s character (~ 3 per cent) is required to give calculated values of the dipole moment of zero.

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Identification of N-2 : 4-Dinitrophenylamino-Acids

IDENTIFICATION of the free amino-groups of proteins by converting them into N-2 : 4-dinitrophenyl derivatives was first introduced by Sanger¹. Since then, several workers have evolved chromatographic methods for the separation of the dinitrophenyl amino-acids.

The regeneration of the parent amino-acid from its dinitrophenyl derivative is desirable both to confirm results from other methods and as a method in itself, since, as is well known, an excellent separation of free amino-acids can be achieved on paper using two solvents. Mills² attempted this by hydrolysing the dinitrophenyl derivatives with saturated baryta in a sealed tube. This method is applicable to the relatively long-chain amino-acids; but in our