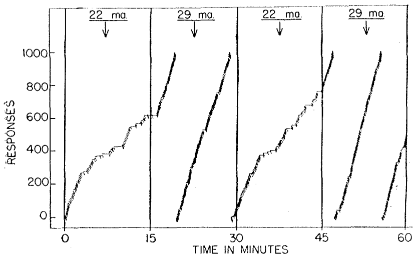

Fig. 2. A 60-minute session under fixed-ratio (8:1) during which the electric stimulus current was varied in alternate 15-minute periods (cat E-5, 7 Mar. 1955).

food and water deprivation, and conditioned "anxiety" states, on behavior controlled by brain stimulation. Reports of these investigations are now in preparation.

M. Sidman
J. V. Brady
J. J. Boren
D. G. Conrad
Neuropsychiatry Division, Army Medical Service Graduate School, Walter Reed Army Medical Center, Washington, D.C.
A. Schulman
Department of Physiology, Yale University School of Medicine, New Haven, Connecticut

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21 June 1955

Proton Affinity of Phosphine in the Phosphonium Halides

It has been pointed out by Grimm (*1*) that it is possible to calculate the proton affinity of ammonia, P_{NH_3}, if the crystal energies of the ammonium halides and the electron affinities of the halogens are known. Using this method, Sherman (*2*) has calculated the proton affinity of ammonia in the ammonium halides and found it to be 221.0, 209.0, 208.6, and 202.7 kcal in NH_4F, NH_4Cl, NH_4Br, and NH_4I, respectively. An average value of 206.8 kcal was adopted. Similar calculations were made for the proton affinity of water, the calculated value being 182 kcal.

Experimental evidence indicates that phosphine is a weaker base than ammonia. The absence of a series of phosphonium salts comparable in stability to the ammonium salts is evidence for the decreased basicity. At room temperature PH_4I is a solid (sublimation point 62°C), while the bromide and chloride are dissociated gases. Since the proton affinity of a molecule is a measure of basicity, it was of interest to calculate this value for phosphine.

The proton affinity of phosphine, P_{PH_3}, is defined as the energy change for the reaction

$$PH_4^+ \rightarrow PH_3 + H^+$$

This energy change can be calculated indirectly by use of the familiar Born-Haber cycle. This cycle is represented as

$$\begin{tikzcd}
& (PH_4X) \arrow[r, "U"] & PH_4^+ + X^- \arrow[dr, "P_{PH_3}"] & \\
\tfrac{1}{4}P_4 + 2H_2 + \tfrac{1}{2}X_2 \arrow[ur, "-Q_{PH_4X}"'] & & & PH_3 + H^+ + X^- \arrow[dll, "-I_H + E_X"] \\
& PH_3 + H + X \arrow[ul, "Q_{PH_3}", "-D_H - D_X"'] & &
\end{tikzcd}$$

The proton affinity at 0°K is given by the relation

$$P_{PH_3} = U + Q_{PH_4X} - Q_{PH_3} + D_H + I_H + D_X - E_X - 5/2RT,$$

where U is the lattice energy of the PH_4X (X representing chlorine, bromine, or iodine) Q_{PH_4X} is the heat of formation of PH_4X, Q_{PH_3} is the heat of formation of phosphine, D_H is the heat of dissociation of hydrogen, I_H is the ionization potential of hydrogen, D_X is the heat of dissociation of the halogen molecule, E_X is the electron affinity of the halogen, and RT is the gas constant, 1.987 cal deg^{-1} mole^{-1}, times the temperature, 298.1°K.

Table 1 gives the thermal data required to calculate the proton affinity of phosphine in PH_4I, PH_4Br, and PH_4Cl. Because of the unreliability of many of the data, the calculated proton affinities are accurate only to about ± 5 percent in PH_4I and about ± 10 percent in the other two halides. The error is of this magnitude because the crystal lattice of PH_4I is the only one known with accuracy (*3*). Similar structures have been assumed for the other two halides. Thus, the PH_4I value for the proton affinity would be the most reliable.

Recent electron affinity values for the halogens E_X (*4*) are lower by about 5 to 7 percent than the values used by Sherman (*2*). This would give a higher proton affinity for ammonia by about 2 to 5 percent. Thus, the new values would be in the range from 226 to 210 kcal. However, even with this revision, the proton affinity of phosphine is of the same order of magnitude as that of ammonia.

Table 1. Proton affinity of phosphine at 0°K

Quantity	PH_4I	PH_4Br	PH_4Cl
U*	131.5†	130.3	132.2
$-Q_{PH_4X}$ (*5*)	15.8	29.5	42.5‡
Q_{PH_3}	2.21	2.21	2.21
$-D_H$	52.1	52.1	52.1
$-I_H$	311.9	311.9	311.9
$-D_X$	25.5	26.7	28.9
E_X (*4*)	74.6 (*6*)	81.5	86.5
$5/2RT$	1.5	1.5	1.5
$-P_{PH_3}$	200 ± 10	209 ± 21	217 ± 22

* Assume a CsCl lattice, densities of PH_4Br and PH_4Cl estimated at 1.94 and 1.27 g/cm^3, respectively.
† All values in kilocalories.
‡ Estimated from the Q_{PH_4Cl} in the gas phase.

The low value for the proton affinity of water would indicate that the H_3O^+ is less stable than the PH_4^+. The reverse seems to be true because the phosphonium halides, unlike the ammonium halides, are readily hydrolyzed by water according to the equation

$$PH_4X + H_2O \rightarrow PH_3 + H_3O^+ + X^-$$

Apparently other factors must enter in, because this result is not what would be predicted according to the calculated proton affinities of water and phosphine.

Wesley Wendlandt
Department of Chemistry and Chemical Engineering, Texas Technological College, Lubbock

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15 March 1955

Ecology and the Population Problem

In commenting on the problem of providing space and food for the growing human population, A. M. Woodbury implies [*Science* **122**, 200 (1955)] that this problem is sufficiently critical in the United States to reduce such questions as those concerning the preservation of our national parks and monuments and recreation areas to the status of "minor matters." Woodbury is my former teacher and companion in fieldwork, and he is the man most directly responsible for my initial decision to become an ecologist; hence, there is no one to whom I would