

THE ROLE OF HYDROGEN BONDS IN CONDUCTION BY HYDROGEN AND HYDROXYL IONS

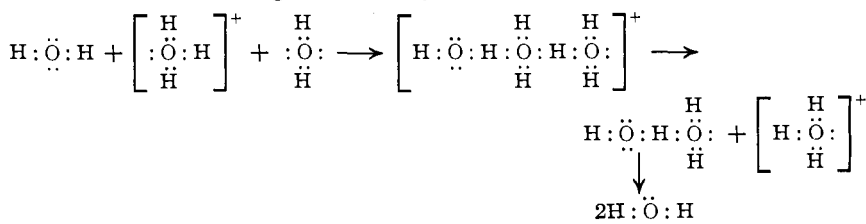
Sir:

The abnormally high conductance of hydrogen and hydroxyl ions in water solution is well known.¹ To account for this it has been proposed² that "an interchange takes place between the ions and the solvent molecules with the result that the mean path over which these ions travel is reduced in proportion to the effective diameter of the solvent molecules which are concerned in this interchange"—a modification of Grotthuss' chain theory of conduction.

Against this hypothesis it has been pointed out¹ that similar abnormally high conductances would be expected for solvent ions in solvents such as ammonia, whereas this is not the case. Recourse is then had to the assumption that the abnormal speeds of the solvent ions in water are due to their relatively low hydration.

I shall attempt to show now that the concept of "hydrogen bonds," first proposed by me in 1919 and shortly thereafter independently by Latimer and Rodebush, furnishes a satisfactory mechanism for chain conduction by the solvent ions in water but not in ammonia.

Let us assume, for simplicity, that hydrogen ions are $\left[\begin{array}{c} \text{H} \\ \text{H} : \ddot{\text{O}} : \text{H} \end{array} \right]^+$ in water and $\left[\begin{array}{c} \text{H} \\ \text{H} : \ddot{\text{N}} : \text{H} \\ \text{H} \end{array} \right]^+$ in ammonia. The hydrogen kernels are held quite tightly to the oxygen and even more tightly to the nitrogen. In the case of H_3O^+ the force holding each hydrogen will be greatly decreased if another hydrogen, say in an H_2O molecule, approaches the lone pair in the oxygen valence shell. If at the same time an oxygen lone pair in another water molecule should approach one of the H_3O^+ hydrogens, that hydrogen might well be transferred to this second water molecule, making it an H_3O^+ ion. Diagrammatically

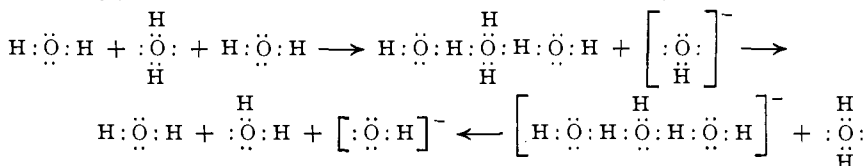


Such a mechanism is obviously impossible with NH_4^+ ions, for no lone pairs are available to aid in the "loosening" of the NH bonds.

¹ Cf. Kraus, "Properties of Electrically Conducting Systems," The Chemical Catalog Co., Inc., New York, 1922, p. 206.

² Lucasse, Thesis, Clark University, 1920.

Analogously, an OH^- ion can remove a hydrogen from a water molecule if the oxygen in the latter has around it three other hydrogens



Although one might postulate hydrogen bonds between NH_3 molecules so as to produce nitrogen atoms surrounded by four hydrogens, these hydrogens would be more tightly held than each of four hydrogens surrounding an oxygen (NH_4^+ is more stable than OH_4^{++}) and apparently they cannot easily be removed by NH_2^- ions.

It seems likely, moreover, that $\text{N} : \text{H} : \text{N}$ bonds are not readily formed. ($(:\text{F} : \text{H} : \text{F} :)^-$ is quite stable; $\text{O} : \text{H} : \text{O}$ bonds are weaker but common in crystals and probably in liquid water and temporarily during many reactions, whereas no examples whatever of $\text{N} : \text{H} : \text{N}$ or $\text{C} : \text{H} : \text{C}$ bonds are known to me.) If so, this in itself suffices to account for the lack of abnormally large conductances of NH_4^+ and NH_2^- in ammonia.

The conductance data for other solvents also seem to be in agreement with the ideas here expressed, but I shall not now take the space to discuss them.

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RECEIVED JULY 15, 1931
PUBLISHED AUGUST 5, 1931

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HEXAFLUORODISILANE

Sir:

Up to the time of the present writing the only binary fluoride of silicon that has been identified definitely is the tetrafluoride, SiF_4 . Methods leading to the formation of so-called subfluorides, several of which have been reported, have failed when repeated by later experimenters. Nevertheless, the presumption remained that binary fluorides other than the tetrafluoride should be capable of existence, since certain of the corresponding compounds of carbon have been isolated.

We have now succeeded in preparing hexafluorodisilane, Si_2F_6 , by gently warming hexachlorodisilane with anhydrous zinc fluoride, followed by condensation and fractionation of the products. The substance is gaseous under ordinary conditions of temperature and pressure, but may be condensed to a snow white solid, melting at -18.5° under 780 mm. pressure.

The vapor pressure of the substance has been determined from -79 to -4° ; the pressure becoming 760 mm. at -19° . Gas density determinations upon the same product lead to the molecular weight 173.8 (calcd. for Si_2F_6 , 170.1). Inasmuch as the product has been shown to be quite pure,