

each other in their intermediate steps. If this were true, it would require a value of $+M/N$ in synthesis of only 0.11 in order to give a steady state at 4.7% NH_3 . That the value for synthesis cannot be so low has been shown above. It therefore appears that the intermediate steps are not independent and that there must be an exchange of activation energy in the direction to produce additional decomposition.

The principal object of this communication is to point out that the shift of equilibrium from that predicted is in the right direction to be accounted for by an exchange of ionization from the elemental ions H_2^+ (16 volts) or N_2^+ (17 volts) to give NH_3^+ (11 volts). Such transfer of ionization would favor decomposition at the expense of synthesis, assuming always that H_2^+ and N_2^+ in some way cause synthesis and that NH_3^+ causes decomposition.

This same type and direction of shift may be general in other similar reactions in gaseous phase, since the larger molecules will usually have a lower ionization potential than either of its components.

An effort is being made to test this hypothesis quantitatively for ammonia by means of a complete kinetic equation which should fit the kinetics of either reaction and the equilibrium.

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THE IONIC NATURE OF THE HYDROGEN BOND

Sir:

In a recent paper, Linus Pauling [THIS JOURNAL, **53**, 1367 (1931)] has pointed out that the hydrogen bond postulated by Huggins, Latimer and Rodebush is to be expected only of molecules having ionic characteristics and that the bond itself is ionic. The evidence that is offered by Pauling is for the most part chemical, and it might be profitable to examine the question in the light of physical data not considered by him.

Work on the Raman effect [in particular Krishnamurti, *Nature*, **125**, 892 (1930)] has indicated that Raman lines are to be expected with atomic bonds (*i. e.*, shared electron pairs) rather than with ionic linkages. The reason for this is obscure; but at least in solutions it may be due in many cases to the magnitude of the energy states involved in the various types of molecules or "resistant groups." Raman data on the association of liquids (such as H_2O , NH_3 and SO_3) are inconclusive so far as offering information about the character of this bond. It might be possible to decide this question from the sharpness of the lines. However, in all of the work that has been done on the Raman effect of hydrates and solutions no lines have been reported that may be interpreted as showing an "atomic vibration" of the water "molecule" with respect to the metal ion. A literal applica-

tion of the older conception of this bond demands that there be such lines. The observed state of affairs is to be expected on the basis of Pauling's suggestion. Furthermore, if the hydrogen ion is connected to the water molecule by means of a shared electron pair in the oxonium ion, we would expect a Raman spectrum characteristic of the latter ion. This would mean that all solutions of acids would have lines in common. An examination of the data for nitric, hydrochloric and sulfuric acids shows that this is not the case.

Another interesting example is the ammonium ion. In solution this ion has no observable Raman lines. This indicates not only that the hydrogen ion connects itself to the ammonia molecule through an ionic linkage, but that in doing so it causes the other bonds to become ionic. It is entirely possible that the case of the oxonium ion is parallel, and that each hydrogen is connected to the oxygen through an ionic linkage.

As investigations in solutions are inherently under adverse conditions, the bond may actually be intermediate in character. At least the evidence indicates quite strongly that it is not of the extreme electron pair type formerly assumed.

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THE CARBON-HALOGEN BOND AS RELATED TO RAMAN SPECTRA

Sir:

The purpose of the work described here was to determine the variation of the characteristics of the bond between carbon and another atom as the length and structure of the hydrocarbon chain is varied. The frequency which corresponds to the carbon-bromine bond in methyl bromide is 1.808×10^{13} per second, but in longer normal chains this is reduced to a constant value of 1.688×10^{13} . In an iso compound or in the presence of a double bond, this is reduced to about 1.61×10^{13} . These frequencies are of considerable interest, since in the simple theory they are supposed to be equal to the frequencies of the carbon-bromine bond in these compounds.

What is sometimes called the "strength of a bond" may be represented by the force constant, which for the carbon-carbon single bond is about 5×10^5 dynes per cm. The values for the carbon-halogen bond do not seem to have been calculated for monohalogenes. They are given in Table I.

The force constant (*a*) is calculated in the ordinary way, and it is considered that the methyl group vibrates as a unit with respect to the halogen atom. In (*b*) a slight, somewhat arbitrary allowance has been made for the fact that this is not strictly true.