paper which were based upon an incorrect extrapolation. The system zinc–tin is certainly abnormal as I pointed out in my original paper in 1923. In this case influences are present which inhibit random orientation of the molecules.

The Hildebrand equation for "Regular Solutions" $RT \ln a_1/N_1 = bN_2^2$ or $RT \ln a_2/N_2 = bN_1^2$ can be strictly true only when the two components have the same surface area per molecule. S_{Tl} exceeds S_{Sn} by only 2%, and this is the reason for the result found by Hildebrand and Sharma that "so far as the variation with N is concerned, this system corresponds perfectly to the definition of a regular system given by the senior author" (THIS JOURNAL, **51**, 66 (1929)].

The evidence presented thus lends support to Langmuir's equation and to the assumptions upon which it is based.

More extensive data and a fuller treatment of this problem will be presented in a later publication.

SCHOOL OF CHEMISTRY   NELSON W. TAYLOR
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA

RADIOCHEMICAL EQUILIBRIUM IN AMMONIA SYNTHESIS

Sir:

The attempt to calculate chemical equilibrium or a steady state attained by alpha radiation from the known yield per ion pair of the two opposing non-thermal reactions was first made for the synthesis and decomposition of water [Lind, *Trans. Am. Electrochem. Soc.*, **34**, 214 (1918)]. The case for ammonia is much more suitable since the system remains entirely homogeneous. The decomposition of ammonia has been measured by Wourtzel [*Le Radium*, **11**, 342 (1919)]. The yield in synthesis was determined in a flow system by Lind and Bardwell [THIS JOURNAL, **50**, 745 (1928)] to lie in the range $+M_{NH_3}/N_{(N_2 + H_2)} = 0.2$–$0.3$. Choosing 0.2 as the most probable value of $+M/N$ and the round number 1.0 (from Wourtzel) for the decomposition $(-M/N)$, Lind and Bardwell calculated that the equilibrium (at 25°) would be $(1.0/1 + 0.2) = 83.3\%$ decomposition, corresponding to *9.09%* NH₃ by volume.

Later Ponsaert [*Bull. soc. chim. Belg.*, **38**, 110 (1929)] redetermined the yield for synthesis as *0.32* and taking 1.08 from Wourtzel for decomposition calculated equilibrium at 13.5% NH₃ by volume. The actual equilibrium has now been experimentally determined by D'Olieslager and Jungers [*Bull. soc. chim. Belg.*, **40**, 75 (1931)] as only *4.7%* NH₃ by volume.

In calculating the equilibrium from the yields at the beginning of the opposing reactions where back-reaction is negligible, it has been assumed that the mechanisms of the two reactions at equilibrium are independent of

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.

School of Chemistry S. C. Lind
University of Minnesota
Minneapolis, Minnesota
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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-