

control experiment seems to be needed: namely, to test the constancy of the emanating power of some other eutectic mixture, prepared in a similar manner, but consisting of salts known definitely not to form any compounds whatsoever, at any temperatures, such as the pair  $\text{KCl-K}_2\text{SO}_4$ . In experiments described by Hahn himself<sup>1</sup> (pp. 200-215), even pure substances, which could not be undergoing any chemical reaction, such as dried thorium oxide or iron oxide gels, show variation of the emanating power on mere standing, at various temperatures, and in various degrees of relative humidity.

Finally, Hahn and Strassmann offer the following explanation for the otherwise surprising reactivity of these dry solid salts at a temperature so far below their melting points. On the basis of the "loosening temperature" of "incipient softening," as observed by Hahn and collaborators in work with the emanation method [a phenomenon similar to the "agglomeration temperature" observed in experiments of Tammann],<sup>5</sup> a preliminary loosening of the crystals of a simple solid is to be expected at a temperature approximately 0.5 to 0.6 of the absolute melting point. Hahn and Strassmann then suggest that their salt mixture was evidently already in the temperature range of this preliminary loosening, inasmuch as 20° is 0.53 of the absolute melting or freezing point, 278°, of the mixture considered as a eutectic. This reasoning however involves a misconception of the meaning of Tammann's "loosening" or "agglomeration" temperature. Materials in a mixture (no matter what the proportion may be—and the proportions of a eutectic mixture are purely accidental) behave independently in respect to strictly thermodynamic properties. The temperature of the preliminary loosening of the crystal lattice is, of course, a function of the lattice itself, or of the lattice bond strengths. This property, for either of the two salts involved in a simple eutectic, remains constant and is not affected by the presence of the merely admixed crystals of the other salt. In a eutectic mixture, in short, as in any mixture of solids, we are dealing with two separate phases, each with its own thermodynamic properties, and its own crystal structure. Consequently the temperature of 20° of the experiment cannot be related to the so-called eutectic melting point but only separately, for each salt, to its own individual melting point, in the calcu-

(5) Tammann, *Z. anorg. allgem. Chem.*, **176**, 46 (1928).

lation of the approximate temperature at which this preliminary loosening may be expected to start; these "loosening temperatures" would then be between 37 and 98° for potassium nitrate and between 161 and 248° for barium nitrate, that is, far above room temperature.

DEPARTMENT OF CHEMISTRY  
NEW YORK UNIVERSITY  
NEW YORK, N. Y.

RECEIVED MARCH 20, 1937

### Exchange Reaction of Organic Compounds with $\text{D}_2\text{SO}_4$

BY RUDOLF SCHOENHEIMER, D. RITTENBERG AND  
A. S. KESTON

Ingold, Raisin and Wilson<sup>1</sup> have found that aliphatic hydrocarbons exchange hydrogen with  $\text{D}_2\text{SO}_4$ . Since this finding offered a possibility of preparing deuterio compounds, we have investigated the exchange of (a) palmitic acid, (b) *dl*-alanine, (c) *d*-leucine, and (d) cholesteryl chloride dibromide. The first three compounds were dissolved in 95-99% sulfuric acid containing 25-30 atom per cent. of deuterium, and heated at 100° for twenty-four hours. The cholesterol derivative not being soluble in sulfuric acid was dissolved in carbon tetrachloride and this solution refluxed in contact with the sulfuric acid. The substances isolated contain (a) 1.78, (b) 1.30, (c) 0.86, (d) 0.03 atom per cent. of deuterium. The leucine was racemized. Neither of the amino acids on boiling with large volumes of 20% ordinary sulfuric acid in  $\text{H}_2\text{O}$  for forty-eight hours lost any of the deuterium introduced by the concentrated  $\text{D}_2\text{SO}_4$ . The fact that the deuterium content of the cholesterol derivative is so small is probably due to its insolubility in sulfuric acid.

(1) C. K. Ingold, C. G. Raisin and C. L. Wilson, *J. Chem. Soc.*, 1643 (1936).

DEPARTMENT OF BIOLOGICAL CHEMISTRY  
COLUMBIA UNIVERSITY  
NEW YORK, N. Y.

RECEIVED AUGUST 2, 1937

### The Ratio of Substitution to Addition in the Reaction of Chlorine with Olefins in Dilute Carbon Tetrachloride Solution

BY T. D. STEWART, KENNETH DOD AND GEORGE STENMARK

Stewart and Weidenbaum<sup>1</sup> found 2-pentene to yield largely 1-chloro-2-pentene upon chlorination and interpreted the substitution as a reaction induced by the normal addition reac-

(1) Stewart and Weidenbaum, *This Journal*, **58**, 98 (1936).