

the purpose of investigating the phase relationships, cannot, of course, be considered complete, the general fact of compound formation is very clear. The reality of the significance of the curve a'-b' for the $\text{Ba}(\text{NO}_3)_2\text{-NaNO}_3$ system becomes even more evident on inspection of the family of curves for the system, shown in the original paper of Harkins and Clark, with various amounts of potassium nitrate added to the binary system; the same is true of the curves for the $\text{Ba}(\text{NO}_3)_2\text{-KNO}_3$ system with various percentages of sodium nitrate present.

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Some Remarks on the Evidence for "Molecular Shift in the Solid State" Adduced by O. Hahn in "Applied Radiochemistry"

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One of the most interesting applications of the "emanation method" presented by O. Hahn in his recent book on "Applied Radiochemistry,"¹ is the attempt to find evidence for molecular shift or mobility in the solid state. This evidence, according to Hahn, rests on two experiments (performed in his Laboratory and published by F. Strassmann),² the more important being an experiment interpreted as proving that a mixture of the salts potassium nitrate, KNO_3 , and barium nitrate, $\text{Ba}(\text{NO}_3)_2$, standing at 20° for five hundred and ten days had undergone a reaction (reaching in fact complete equilibrium) resulting in the formation of the compound $\text{Ba}(\text{NO}_3)_2\cdot 2\text{KNO}_3$ plus excess of potassium nitrate. This interesting and surprising experiment is found, however, on careful inspection, to have been faulty, not only in the premises on which its conclusions were apparently based (in respect to the relationships in the binary system $\text{Ba}(\text{NO}_3)_2\text{-KNO}_3$) but also in its scientific strictness and in the logic of the "explanation."

The experiment referred to may be described, briefly, as follows. Accepting apparently the data of Guthrie³ (1884) on the binary system as a basis—although the reference is not stated—a mixture of the two salts containing 29.53% of barium nitrate into which had been incorporated a trace of radium nitrate, and melting at 278°

(these are the exact values of Guthrie's eutectic), was melted and cooled; the powdered solid was then allowed to stand at room temperature for five hundred and ten days, during which time the emanating power was found to decrease from 8.1 to 1.3%, indicating, according to the principle of the emanation method, a decrease in the effective surface area of the crystals. Assuming that the original mixture was an ordinary eutectic mixture of the two simple salts, it was then inferred on the basis of these measurements that the salts had obviously reacted to form the well-known double salt $\text{Ba}(\text{NO}_3)_2\cdot 2\text{KNO}_3$, to account for what may be called the "setting" of the crystals. To "prove" this hypothesis, some of the material, which had been standing for five hundred and ten days and the emanating power of which had dropped to about 1%, was ground still further and subjected to a centrifugal fractionation, in which it divided itself into two portions, one being practically pure potassium nitrate and the denser fraction containing all the barium nitrate and analyzing to 56.2–56.8% $\text{Ba}(\text{NO}_3)_2$, in very good agreement with the theoretical composition 56.4% $\text{Ba}(\text{NO}_3)_2$ calculated for the compound $\text{Ba}(\text{NO}_3)_2\cdot 2\text{KNO}_3$; it is to be noted that this would imply not merely an "incipient conversion of the mixture to the double salt," but a complete reaction which has reached equilibrium. This circumstance in itself points to the high probability that the original mixture did not consist of the simple salts, but already contained the compound later found.

The whole experiment rests of course on the assumption that the original solid was a mixture of the simple separate salts and not of double salt plus excess potassium nitrate. As pointed out, however, in a preceding note,⁴ the molten salts barium nitrate and potassium nitrate form at least one definite compound, $2\text{BaNO}_3\cdot\text{KNO}_3$, and possibly a second of the composition $\text{Ba}(\text{NO}_3)_2\cdot 2\text{KNO}_3$, so that the eutectic mixture was already a mixture of potassium nitrate plus one or the other of these compounds, more probably the latter. Actually then there is no evidence in this experiment of any reaction whatever in the solid state. If the centrifuging treatment had been applied at once to the original solid mixture, without doubt the same separation later obtained into potassium nitrate and the compound, would have resulted. Still another

(1) Otto Hahn, "Applied Radiochemistry," Cornell University Press, Ithaca, N. Y., 1936; see especially pp. 226–232.

(2) F. Strassmann, *Z. physik. Chem.*, **B26**, 353 (1934).

(3) Guthrie, *Phil. Mag.*, [5] **17**, 462 (1884).

(4) Ricci, *THIS JOURNAL*, **59**, 1763 (1937).

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 himself¹ (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],⁵ 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-

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.

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Exchange Reaction of Organic Compounds with D_2SO_4

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Ingold, Raisin and Wilson¹ have found that aliphatic hydrocarbons exchange hydrogen with D_2SO_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 H_2O for forty-eight hours lost any of the deuterium introduced by the concentrated D_2SO_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).

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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 Weidenbaum¹ 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-

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

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