brought into contact with this surface an increase of 3.3 Å. was observed which disappeared, however, within five minutes. This increment would indicate a lengthwise adsorption independent of length of chain.

The ability of a thorium nitrate or aluminum chloride solution to condition the surface of a multilayer depends upon the composition of the built-up film. A mixed barium stearate–stearic acid film containing 50% or more of stearate is conditioned more readily than a film of pure stearic acid. Films of copper stearate from water containing 1×10^{-5} *M* copper chloride or a barium stearate layer covered by an A-X monolayer of oleic acid do not react at all with either the thorium or aluminum solution.

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Compound Formation in the Binary Systems $Ba(NO_3)_2$–KNO_3 and $Ba(NO_3)_2$–$NaNO_3$

BY JOHN E. RICCI

In connection with a discussion appearing in a subsequent note,[1] the existing data on the binary systems $Ba(NO_3)_2$–KNO_3 and $Ba(NO_3)_2$–$NaNO_3$ have been re-examined critically, with the conclusion that whereas both systems have heretofore been represented as of the simple eutectic type, the data actually indicate definite compound formation in both cases.

Aside from incidental measurements by Maumené[2] and by Guthrie,[3] the only phase rule studies of the binary systems $Ba(NO_3)_2$–KNO_3 and $Ba(NO_3)_2$–$NaNO_3$ appear to have been made by Harkins and Clark[4] and by Laybourn, Madgin and Freeman.[5] No double salt formation was reported in either of these latter investigations. The summaries, edited by Amadori, given in the "International Critical Tables,"[6] are those of Harkins and Clark, so that the same statements appear there too. Of these two studies, the earlier, that of Harkins and Clark, is more nearly complete in data, although no inferences at all were drawn as to the phases present. The later work of Laybourn, Madgin and Freeman, which apparently verified the system to be simple, must, in the writer's opinion, however, be considered inconclusive both in the light of a careful inspection of the data of Harkins and Clark, and because of the incomplete range of composition covered: only 0–47 mole % $Ba(NO_3)_2$ in the potassium system, and only 0–40 mole % $Ba(NO_3)_2$ in the sodium system.

The data of Harkins and Clark, recalculated into mole percentages, as listed in the "International Critical Tables,"[6] are used in plotting the freezing point diagrams for the two systems shown in Fig. 1.

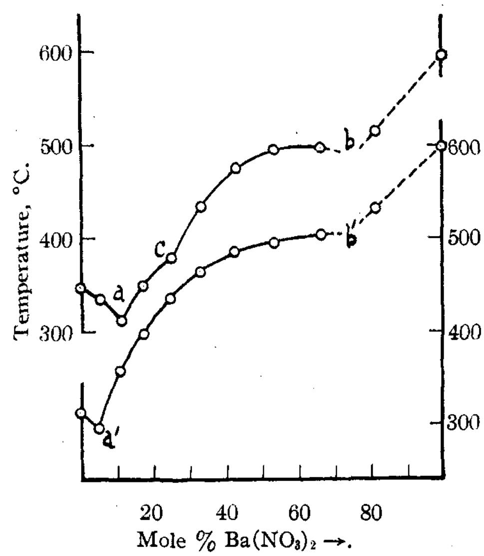

Fig. 1.—Freezing point diagrams for systems $Ba(NO_3)_2$–KNO_3 (upper curve) and $Ba(NO_3)_2$–$NaNO_3$ (lower curve) from data of Harkins and Clark.

The evidence of compound formation is unmistakable. From the configuration of the respective curves a–b and a′–b′ of the two systems, the probable formulas of the compounds involved may be given as $2Ba(NO_3)_2$–KNO_3 and $2Ba(NO_3)_2 \cdot NaNO_3$. The single point c of the potassium nitrate system, unless due to experimental error, seems to show a further break in the curve of the compound; if this is real, it points to a second compound in the system with the probable formula $Ba(NO_3)_2 \cdot 2KNO_3$. Although a single point can hardly be considered sufficient ground for such an inference, it must be mentioned that the existence of the latter compound in the ternary system $Ba(NO_3)_2$–KNO_3–H_2O is well established.[7]

In conclusion, although the measurements of Harkins and Clark, which were not performed with

(1) Ricci, THIS JOURNAL, **59**, 1764 (1937).
(2) Maumené, *Compt. rend.*, **97**, 1215 (1883).
(3) Guthrie, *Phil. Mag.*, [5] **17**, 462 (1884).
(4) Harkins and Clark, THIS JOURNAL, **37**, 1816 (1915).
(5) Laybourn, Madgin and Freeman, *J. Chem. Soc.*, 139 (1934).
(6) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., Vol. IV, 1928, p. 66.
(7) Glasstone and Riggs, *J. Chem. Soc.*, **127**, 2846 (1925).

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 $Ba(NO_3)_2$–$NaNO_3$ 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 $Ba(NO_3)_2$–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"

BY JOHN E. RICCI

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, $Ba(NO_3)_2$, 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 $Ba(NO_3)_2 \cdot 2KNO_3$ 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 $Ba(NO_3)_2$–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 Guthrie[3] (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 $Ba(NO_3)_2 \cdot 2KNO_3$, 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% $Ba(NO_3)_2$, in very good agreement with the theoretical composition 56.4% $Ba(NO_3)_2$ calculated for the compound $Ba(NO_3)_2 \cdot 2KNO_3$; 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, $2BaNO_3 \cdot KNO_3$, and possibly a second of the composition $Ba(NO_3)_2 \cdot 2KNO_3$, 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).