dioxide evolved was less than could be estimated (0.1–0.2 mml.).

α-Amino-*p*-methoxyphenylacetic Acid.—From the reaction mixture an aldehyde fraction consisting of benzaldehyde and anisaldehyde was isolated as a mixture of the 2,4-dinitrophenylhydrazones, m. p. 231–233°. The corresponding derivatives of benzaldehyde and anisaldehyde melt at 242–243° and 255°, respectively. The yield of hydrazones calculated as benzaldehyde was 0.5 mml. A methoxyl determination showed 3.5% OCH$_3$, indicating a mixture of 64% benzaldehyde and 36% anisaldehyde. The amino acid fraction (8.0 mml.) consisted chiefly of aminomethoxyphenylacetic acid (OCH$_3$, 15.64; N, 7.43).

Cystine.—No benzaldehyde nor hydrogen sulfide could be detected. From the reaction mixture about 0.5 mml. of α-aminophenylacetic acid was isolated after removal of the last traces of cystine by treatment with lime and lead acetate.

S-Ethylcysteine.—During twelve hours only 0.7 mml. of carbon dioxide was formed. From the bisulfite trap a small quantity of ethylthioglycolic aldehyde was isolated. Neither benzaldehyde nor acetaldehyde could be identified as reaction products.

Summary

The investigation of the reaction between α-amino acids and α-ketonic acids has been extended in such a manner as to demonstrate more clearly the mechanism involved. The first steps in the reaction appear to lead to the formation of a Schiff base with a carboxyl group on each of the carbon atoms adjacent to the central nitrogen atom. The double bond of the methyleneazomethine system has a tendency to shift (C—N=C $\longrightarrow$ C=N—C) with the simultaneous elimination of carbon dioxide from either carboxyl group, both processes being dependent upon the nature of the other carbon substituents. In the case of α-amino-α-phenylbutyric acid this tendency is so pronounced that it takes place in spite of the necessity of forcing the displacement of the carboxyl group. Two new Schiff bases are assumed to result. Of these, one hydrolyzes to give the original amino acid and the aldehyde formed by decarboxylation of the ketonic acid; the other decomposes to form a new amino acid, derived from the ketonic acid by amination and reduction, and the aldehyde resulting from the oxidative deamination and decarboxylation of the original amino acid.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Further Observations Concerning the Crystallization of Undercooled Liquids

BY WILLIAM T. RICHARDS, EDWARD C. KIRKPATRICK AND CARL E. HUTZ

Introduction

The belief that homogeneous crystallization[1] of metastable liquids could be described successfully in statistical terms originated with the Kinetic Theory of Heat. With the writings of de Coppet, Ostwald and Tammann, which are too well known to require summary here, this belief became increasingly articulate. Recently Volmer[2] and Stranski[3] have expressed it in terms of Fluctuation Theory, and theoretical aspects of homogeneous crystallization have now advanced as far as the imperfect state of the Kinetic Theory of Liquids permits. Experiment has failed to keep pace with this development. A few cases of homogeneous crystallization, notably those described by Tammann[4] in very viscous melts, where the linear crystallization velocity is extremely small, have been reported. In general, however, a considerable body of scattered experimental work has served only to confuse the issue by the introduction of heterogeneous effects. The mechanism of heterogeneous crystal nucleus formation presents, however, certain points of interest in its own right, although the language for its description is at present less unequivocal and aesthetic than that for homogeneous crystallization. When the immense practical importance of the problem of efficiently inducing crystallization in metastable liquids, affecting, as it does, most organic preparations and many technical processes, is recalled it will be clear that any investigation concerning crystallization which contributes to the present knowledge, however imperfectly its results may be formulated, deserves attention. The object of the present communication was initially to determine the homogeneous crystallization rates of a number of liquids. It was found necessary, however, to interpret the re-

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[1] The term "homogeneous crystallization" will be used throughout to designate crystallization occurring in the free liquid, as opposed to "heterogeneous crystallization" which occurs at an interface.

[2] M. Volmer, *Z. Electrochem.*, **35**, 55 (1929).

[3] I. N. Stranski and R. Kaischew, *Z. physik. Chem.*, **B26**, 100, 317 (1934).

[4] G. Tammann, "Kristallisieren and Schmelzen," 1903.

sults in heterogeneous terms. This interpretation is incomplete in many respects but, since independent experiments from Germany have appeared during the progress of the investigation, it has been decided to report its present status, indicating in the discussion the directions in which future progress appears most probable. As an introduction a brief *résumé* of various heterogeneous effects which have been reported will be given. This review can, owing to the scattered and usually wholly independent investigations with which it deals, make no claim to completeness.

It was Tammann himself who first threw serious doubt upon the homogeneous mechanism, although he does not appear to have been willing to accept the full implications of his work. He reported that, with betol, quartz powder greatly increased the number of crystal nuclei and that powdered glass effectively prevented their formation.[5] Simultaneously Schaum reported that tubes of benzophenone showed a marked decrease in their tendency to crystallize with increasing number of meltings;[6] this phenomenon of "aging" will receive further attention below. Continuing his studies with Schoenbeck, Schaum then demonstrated that crystallization repeatedly occurred at the same spots, and that these spots could be deactivated with increased heating above the melting temperature.[6a] Similarly Jaffé showed that mechanical cleaning, such as intensive filtration, served to increase the range of temperature in which a solution could be maintained in a supersaturated condition,[7] and Füchtbauer extended these observations to undercooled liquids.[8] Both authors seem clearly to have recognized the heterogeneous character of the process of crystal nucleus formation, and Füchtbauer cites the effect of preheating noticed by Schaum and Schoenbeck, although apparently unconscious of earlier work on the subject. Young and Burke,[9] R. Marcelin,[10] Hinshelwood and Hartley[11] and Schaum and Riffert[12] independently not only of each other but of most previous work in the field, have described various aspects of the effect of preheating, and appear to agree that the crystallization center is situated on an interface of some sort. In apparent contradiction to this Orthmer[13] and Kornfeld[14] report a statistical distribution when the crystallization of a large number of samples was observed for long periods of time. Orthmer, however, admits the influence of foreign solids without attempting to account for it. It is believed that these various findings have been successfully explained by a communication from this Laboratory[15] in which it was demonstrated not only that the presence of overheatable nuclei was due to the presence of an interface but that, by the introduction of suitable solid adsorbents which had previously been infected with crystalline material, the number of crystal nuclei could be increased to almost any extent desired. A theory was given based upon the existence of two hypothetical modifications of the adsorbate which were called "crystalline"[16] and "liquid," respectively. Several consequences of the theory, especially its implication that crystal nuclei could be developed above the melting temperature, were confirmed experimentally. The subsequent publications of Biilmann and Klit[17] and Roginsky, Sena and Zeldowitsch[18] confirm this standpoint, and it does not at present appear to require modification.

Two questions remain unanswered by the work which has been summarized above. When the "crystalline adsorbate" has been destroyed by heating until all overheatable germs have disappeared, will crystallization take place in a homogeneous and consequently statistical manner? If not, is there a connection between the presence of adsorbents which contribute to the formation of overheatable germs and the process of crystallization, even when the overheatable germs themselves have been destroyed? It is believed that conclusive negative answers to both these questions may be inferred from the evidence presented below.

Experimental

The experiments were conducted with a large number of tubes, usually about a hundred, which were immersed si-

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[5] G. Tammann, *Z. physik. Chem.*, **25**, 441 (1898).

[6] K. Schaum, *ibid.*, **25**, 722 (1898).

[6a] K. Schaum and F. Schoenbeck, *Ann. Physik.*, **8**, 652 (1902).

[7] G. Jaffé, *Z. physik. Chem.*, **43**, 565 (1903).

[8] C. Füchbauer, *ibid.*, **48**, 549 (1904).

[9] S. W. Young and W. E. Burke, This Journal, **29**, 329 (1907).

[10] R. Marcelin, *Compt. rend.*, **148**, 631 (1910).

[11] C. N. Hinshelwood and H. Hartley, *Phil. Mag.*, **43**, 78 (1922).

[12] K. Schaum and P. Riffert, *Z. anorg. allgem. Chem.*, **120**, 241 (1922).

[13] P. Orthmer, *Z. anorg. Chem.*, **91**, 209 (1915).

[14] G. Kornfeld, *Monatsh.*, **37**, 609 (1916).

[15] W. T. Richards, This Journal, **54**, 479 (1932).

[16] The term "crystalline adsorbate" is not here intended to imply identity in structure with that of the crystal, but merely a variety of the adsorbate which yields the crystal on contact with free undercooled liquid.

[17] E. Biilmann and A. Klit, *Kgl. Danske. Videnskb. Selskab Math.-fys. Medd.*, **12**, 1 (1932).

[18] S. Roginsky, L. Sena and J. Zeldowitsch, *Phys. Z. Sov.*, **1**, 630 (1932).

multaneously in a constant temperature bath. They were then photographed on successive single frames of a 16-mm. motion picture camera at intervals of four minutes. A telechron motor, fitted with appropriate gears and contacts, provided that the bath should be stirred for three minutes and fifty seconds; the stirring was then discontinued and the illumination switched on, and, after ten seconds in which the agitation of the bath subsided, the picture automatically taken. The cycle then began anew. The apparatus was capable of functioning continuously for weeks without failure. The thermostat was a Dewar flask of about 20-liters capacity, and the tubes were held in this by a black Bakelite rack perforated to receive 100 tubes, each of which contained about 10 cc. of undercooled liquid. The photographic negative revealed clearly the difference between crystallized and uncrystallized material although it did not generally permit the location of the point at which crystallization began. Several other pertinent objects such as a clock, written information concerning the nature and conditions of the determination, etc., were also photographed. Thus, in the relatively small compass of a few feet of film, a complete record of the performances of each tube in a determination could be secured. A detailed record of this character would have been essential if statistical crystallization had been found; actually visual observation often provided sufficient evidence more conveniently.

Experiments were carried out with four substances. Salol, of the U. S. P. grade, was studied without attempt at purification. Several sources provided different samples of salol, but, in spite of minor variations in the melting point, the behavior of the various samples was uniform. Benzophenone, which had been twice distilled *in vacuo* with as little ebullition as possible, was also employed. Benzene, initially of the reagent grade, was shaken successively with sulfuric acid, dilute sodium hydroxide and water. It was then twice distilled from phosphoric anhydride. Purified carbon tetrachloride was also used, but since it was found to crystallize in too narrow a temperature range to permit differentiation in the behavior of individual samples, experiments with this substance will not be reported. The tubes were of Pyrex glass, and were steamed out for five minutes each by a jet of live steam, and dried at 110° by blowing in clean compressed air. They were evacuated and sealed after being filled with liquid. Ordinary cleanliness was maintained during their filling, but especial precautions to exclude dust were taken only in one case, which will receive individual mention below.

In reporting the experimental findings two alternatives are possible, neither of which is wholly satisfactory. Either detailed accounts of each of the various experiments may be given, or the general conclusions from a group of experiments may alone be stated. The first method would fill an immense amount of space with virtually unreadable material and, since the results are clearly not reproducible in detail, the space would largely be wasted. The second suppresses the facts and places too much emphasis on the judgment of the experimenters; details of importance may thus be lost by oversight. It has been decided to adopt the second alternative and to state the results in a series of conclusions, for which the experimental basis will be sketched only briefly. The reader is cautioned that few of these conclusions are wholly without exception; none, however, have been stated which do not represent an overwhelming majority of cases. A few specific experiments, which are not easily generalized in this way, will then be cited.

1. All samples of salol, benzophenone and benzene could be crystallized by immersing in a slush of solid carbon dioxide and acetone, and returning slowly to room temperature. (It will be apparent in the discussion why this seemingly obvious statement is included.)

2. Ten per cent. of the salol and benzophenone samples and 50% of the benzene samples could be activated by low temperature crystallization to produce crystals at relatively small undercoolings. For example 8 of 94 tubes containing benzophenone could be undercooled at −17° for twenty-four hours, and would remain apparently indefinitely at room temperature, without crystallization. After crystallization in a carbon dioxide–acetone mixture they could be heated to 100° and yet would crystallize within twenty-four hours at room temperature. A temperature of 140° was, however, sufficient to destroy this activity. Similar behavior with salol and benzene was found. Activity of this kind was destroyed with benzene, however, at about 25°, and, when present, manifested itself by permitting only two or three degrees of undercooling. This type of behavior is believed to depend on the presence or destruction of a "crystalline adsorbate."[15]

3. Crystallizations were conducted at various temperatures with each substance to determine a convenient temperature for a large number of identical determinations. Such a temperature was low enough to ensure the crystallization of at least half the tubes within forty-eight hours, and yet not so low that 15% of the tubes crystallized in the first hour. This permitted the establishment of a definite order of crystallization in the case of each substance. The temperatures were: salol −5°, benzophenone −17°, benzene −4°.

4. Repeated crystallizations at these temperatures showed, in agreement with the result which led Hinshelwood and Hartley[11] to postulate a heterogeneous mechanism, that initially the rate of

crystallization was three to ten times that reached after a few hours. A fairly constant rate was sometimes established after the first burst of activity, but it is believed that this is without significance.

5. Each sample behaved in an extremely individual and surprisingly consistent manner. For example, some six of the first ten to crystallize were almost always the same. Some 20% of the total number never crystallized at the temperature specified in the last sentence of (3) and these were also consistently the same samples. Among the intermediate cases the order of crystallization was surprisingly consistent throughout. It is believed, therefore, that a heterogeneous mechanism is responsible for crystallization in all three liquids at these temperatures.

6. No correlation could be found between the ability to form overheatable nuclei, as described in (2), and outstanding rapidity of crystallization at low temperatures. The lack of correlation between the two types of crystallization was, indeed, so striking that no doubt can remain that a different mechanism is involved in the two cases.

A few additional experiments also should be reported.

In the hope of eliminating dust, fifty tubes containing benzophenone which had been filled *in vacuo* in a mammoth all-glass apparatus from twice vacuum-distilled benzophenone were studied. Their behavior differed in no important respect from those filled in the air without special precautions.

The effect of the addition of washed powdered glass and cleaned active charcoal to salol and to benzophenone was also studied. Powdered glass served slightly to increase the tendency to crystallize, and active charcoal very greatly increased it in both cases. It should be added that these substances were added to samples which showed total inability to crystallize under ordinary conditions.

One experiment with benzene also should be cited. After 30% of the samples had crystallized at −4° all tubes were placed in a bath at +17° for twelve hours. On re-immersion in the bath at −4° all thirty of the previous tubes plus fourteen more (44% of the total 100) had crystallized within five minutes. This appears to indicate a slow formation on the adsorbent even above the melting temperature of a form of adsorbate favorable to crystallization.

Discussion

The experiments outlined above lead inescapably to the conclusion that crystallization from undercooled liquids proceeds commonly by a heterogeneous, not by a homogeneous, mechanism. Although only three substances have been studied, two represent the unusual liquid which permits great undercooling, and one the typical symmetrical compound which can be undercooled only a few degrees. There can be little question, therefore, of the generality of the results. As a consequence it is necessary to limit the applicability of any theory describing homogeneous crystallization to very viscous liquids in which the crystal growth velocity is small enough to permit the spontaneous formation of a large number of nuclei before a few of them have grown to sizes which are comparable with the total volume of liquid. It is necessary furthermore to suppose that the "nucleation numbers" found by Tammann, which for thirty years have formed the ground-work for discussion of the subject, are not natural constants but represent only the properties of the particular combination of interfaces which happened to constitute the system which he was observing. Finally, it is indicated inescapably that investigations like the present one, where the crystallization of a large number of tubes is studied as a function of time in the hope of establishing a significant crystallization rate at a given temperature, do not give results which characterize the liquid.

It is, indeed, a questionable matter whether a liquid composed of highly unsymmetrical molecules unconfined by solid surfaces would be capable of forming the solid phase by thermal fluctuations within a reasonable time. In this connection a recent series of papers by Meyer and Pfaff[19] which greatly extend the work of Jaffé and Füchtbauer cannot receive too great attention. These investigators have shown that, by employing sintered glass filters passing particles of 1.5 μ or less, water which may be undercooled 33°, and benzophenone and salol which may be vitrified and returned to room temperature without crystallization, may be obtained. It is the stated belief of these writers that crystallization ordinarily occurs on minute dust particles of unspecified composition, and that removal of the dust precludes the possibility of crystallization.

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[19] J. Meyer and W. Pfaff, *Z. anorg. allgem. Chem.*, **217**, 257 (1934); **222**, 382 (1935); **224**, 305 (1935). A recent paper on water by G. Tammann and A. Büchner, *ibid.*, **222**, 371 (1935), expresses agreement with this standpoint.

To this point of view the investigation reported above contributes the following additional facts. The crystallization centers vary greatly in activity. They are so few in number that two 10-cc. portions of a liquid poured into separate tubes, with an effort to have all conditions identical may comport themselves wholly differently. This is doubtless also the reason for the aging effects so often described. The low-temperature crystallization centers bear no direct relation to the type of adsorption which permits the formation of overheatable nuclei, although carbon appears to be active in both respects. Finally, it is necessary to suppose that the walls themselves can assist in the formation of crystal centers, since dust-free benzophenone, obtained by distillation *in vacuo*, showed no more uniformity than that prepared without special precautions. It should be mentioned in this connection that Meyer and his associates, who were especially concerned with obtaining great undercooling, flamed their glassware intensively before introducing the liquid, whereas we merely cleaned it as described above. This may be the reason why they found no nuclei due to the presence of the containing vessel.

Attempts to account for this behavior must at present be disagreeably speculative. The crystallization centers are so small and so few in number that they defy direct study. It is natural to speak of oriented adsorption of liquid molecules at the interface, but to do so is little more than to give a resounding name to ignorance. The picture outlined in this paragraph is therefore presented in the most humble and tentative spirit, and is included merely to show that one type of adsorptive force is sufficient to account both for the retention of the "crystalline adsorbate" and for the apparently wholly unrelated activity in forming the crystallization centers at low temperatures. Let us consider a wedge-shaped crevice on the surface of the adsorbent. The adsorption forces will be strongest at the bottom of this crevice and become progressively weaker as the surface is approached, as Polanyi[20] and others have shown. Let us further suppose that the adsorbate molecules are oriented in the crevice in much the same way that fatty acid molecules are oriented by glass;[21] this assumption can scarcely meet with objection. Finally let us assume, entirely *ad hoc*, that this orientation causes the adsorbate to resemble the crystal increasingly as the orientation increases; let us suppose, in other words, that the orientation provides the greater part of the surface work, work necessary for the destruction of molecular aggregates, etc., which together may be called the "activation energy of crystallization."[22] Now the conditions are such, in the type of investigation reported above, that the entire liquid will crystallize from a single nucleus in a time much shorter than that necessary for the nucleus to become active. The portion of the adsorbate which most rapidly can project crystals into the free liquid will then cause the crystallization of the entire liquid. The lower the temperature, in the range with which we are at present concerned, the greater the instability of the undercooled liquid and the less the orientation of the adsorbate necessary to produce crystallization. But it already has been inferred from experimental evidence that the rate of rearrangement in the adsorption space is extremely slow.[15] In terms of the present over-simplified picture this involves the rearrangement of molecules bound by powerful adsorptive forces in a crevice of molecular dimensions. It is in all probability, however, exactly these molecules which form the overheatable nuclei. This may be inferred both from the high temperatures necessary to destroy them, and from the fact that weeks must sometimes elapse before they manifest their presence. If all this is granted as plausible, it is not surprising that the strongly bound molecules cannot project crystals into the free liquid with the rapidity of their more loosely bound neighbors, even though the energy conditions may favor them.

The course for future investigations is clear. There is little to be gained at present in multiplying experiments of the type which are here recorded. Rather, a detailed study should be made of the various surfaces which most effectively contribute to the formation of crystallization centers. This should embrace not only a wide variety of substances, but also as great variations in surface configuration and particle size as possible. The information so accumulated should, on the one hand, permit the elimination of heterogeneous effects in crystallization and, on the other, contribute vitally to the important practical problem of securing the crystallization of difficultly crystallizable liquids.

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(20) M. Polanyi, *Trans. Faraday Soc.*, **28**, 316 (1932).

(21) J. J. Trillat, "Les Applications des Rayons-X," 1931.

(22) M. Volmer and M. Marder, *Z. physik. Chem.*, **A154**, 97 (1931).

We are indebted to Mr. A. L. Loomis of Tuxedo Park, N. Y., for helpful advice concerning the photographic device described in the Experimental Section.

Summary

It has been shown that salol, benzophenone and benzene crystallize spontaneously by a heterogeneous mechanism even in the absence of overheatable nuclei. The tendency to form overheatable nuclei and the spontaneous tendency to crystallize, appear to be entirely unrelated, since the former may be destroyed by heating without affecting the latter. A tentative mechanism is suggested whereby one type of absorptive force might result in both forms of activity. The study has been related to previous investigations on the subject.

PRINCETON, N. J. RECEIVED JULY 7, 1936

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON]

Phase Equilibrium Relationships in the Binary System, Sodium Oxide–Boric Oxide, with Some Measurements of the Optical Properties of the Glasses

BY G. W. MOREY AND H. E. MERWIN

The literature contains a number of observations on some of the compounds in the system, Na_2O–B_2O_3, which will be referred to in connection with those compounds, but there has been no systematic study of the system as a whole, except that by Ponomareff,[1] the results of which are as near correct as would be expected from his experimental method.

Most of the information relating to the phase equilibrium relations in the system was obtained by the usual quenching method. In this method a small sample of the material, usually in the form either of a homogeneous glass, or the product obtained by crystallizing such a glass, is held at constant temperature long enough for equilibrium to be attained, then cooled quickly enough to freeze that equilibrium. The quenched charge is then examined with the petrographic microscope. If it originally contained crystals and has become all glass, the temperature of heat treatment was above the liquidus; if both crystals and glass, below the liquidus. The crystals may be positively identified by their optical properties, and thus assurance given as to the crystalline phase present. The quenching method is preferred by experienced workers whenever it can be applied, but in some cases crystallization takes place so rapidly that the melt cannot be quenched. In such cases recourse must be had to the method of heating curves, and it was necessary to study the metaborate in this manner. The heating-curve method can give good results with sodium diborate, when the necessary care is exercised, as was shown by Day and Allen;[2] and it has been applied by the present authors to sodium tetraborate with satisfactory results. With intermediate mixtures, however, the heating-curve method is of doubtful assistance.

Preparation and Analysis of Materials

The raw materials used were sodium carbonate, borax ($Na_2O\cdot 2B_2O_3\cdot 10H_2O$) and boric acid ($H_3BO_3$). The sodium carbonate was from a specially purified stock which contained less than 0.009% $Fe_2O_3 + Al_2O_3$. The borax and boric acid were from several sources, but were purified by recrystallization before using. The mixtures were made by adding sodium carbonate or boric oxide to fused $Na_2O\cdot 2B_2O_3$, with careful mixing, and the composition was usually known from the synthesis having been carried on under controlled conditions.

The composition of some of the mixtures was established by analysis, using a novel method. It was found that when a mixture of $Na_2O + B_2O_3$ containing an excess of boric oxide over the ratio of 1:1 was evaporated on the steam-bath with hydrofluoric acid, it was changed quantitatively to sodium borofluoride, $NaBF_4$. The properties of this compound will be discussed by us in another place. For our present purpose, it is sufficient to say that it can be dried to constant weight at 110°, and that numerous checks made by converting it to sodium sulfate established its constancy of composition. It melts, with some decomposition, at 373°. The original weight can be restored by adding a little boric acid and again evaporating with hydrofluoric acid. For example, a sample of borax, prepared by recrystallization of a commercial preparation and dehydra-

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(1) J. F. Ponomareff, *Z. anorg. allgem. Chem.*, **89**, 383 (1924); *J. Soc. Glass Techn.*, **11**, 39 (1927). The second reference apparently represents no new experimental work, contains several errors, *e. g.*, p. 43, where the compound $Na_2O\cdot 7B_2O_3$ is claimed, probably a misprint for $Na_2O\cdot 4B_2O_3$, and without justification claims the crystallization of B_2O_3, reproducing in support a picture of a crystal given in the earlier paper as $Na_2O\cdot 4B_2O_3$.

(2) "The Isomorphism and Thermal Properties of the Feldspars," by Arthur L. Day and E. T. Allen, Carnegie Institution of Washington, Publ. No. 31, 1905, p. 29.