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19. KEY WORDS (Continued)

Isomorphism Isothermal cocrystallization Mixed crystals

Synthesis of solid solutions Synthesis of mixed crystals

20 ABSTRACT (Continued)

a procedure normally utilized in phase rule chemistry in studying the behavior of a salt pair in a solvent such as water at constant temperature. Three types of isomorphous solid solutions were the object of principal concern, namely the AP-KP, AP-AN, and AN-KN pairs. Published phase rule data on the ternary system of the above three respective salt pairs in water were used as a basis for making solid solutions of selected compositions. New techniques were devised and tested successfully for making larger quantities than would normally be possible by the strict phase rule approach. In some cases, particularly with the AP-AN solid solutions, the desired degree of product homogeneity was difficult to attain. Effectiveness of the grinding operation of the product, as it was being formed, proved to be of critical importance in the attainment of product homogeneity. Solid solutions of the above-mentioned types were successfully prepared for characterization studies,

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INTRODUCTION

Since the advent of intense international missile rivalry, propellant chemists have been continuously searching for improved ingredients to use in their formulations. A great deal of attention has been directed toward finding new oxidizers for use with solid propellants. On the basis of weight, this component is nearly always the principal one in a solid propellant grain. It is in fact the primary energy source. Frequently, relatively small gains in the properties of a solid propellant can be translated into rather dramatic improvement in characteristics and performance of a rocket system. The chemistry of oxidizers has been exploited extensively, and progress has become increasingly more difficult. Nevertheless, because of the pressing need for better materials, continuing research along these lines has been necessary. For this reason a new approach was sought for the development of improved oxidizers.

The idea was conceived so that stabilizing an otherwise unstable inorganic crystalline oxidizer might be possible by isomorphous substitution of its ions into a more stable, compatible, host crystal. The composite structure could then be regarded as an isomorphous solid solution or oxidizer "alloy." An example of how such a mixed crystal can be formed is as follows:

$$x AB + y AC \longrightarrow (A_{x+y} B_x C_y)$$

(where AB and AC are isomorphous crystals having a common cation A^{T}). The overall effect is equivalent to the substitution of a foreign anion C into the host lattice $A^{T}B^{T}$. This process can be illustrated schematically as follows:



(Host crystal)

(solid solution)

The subject of solid solutions in relation to the inorganic solid state has been discussed by Wells (ref. 29). It is subclassification of a more general phenomenon, namely the defect solid state (ref. 30). Formation of solid solutions is favored if the individual components are related isomorphously (ref. 16). A classic example of an oxidizer solid solution is Hantzsch's compound (ref. 7), which was thought to be a salt with a formula $HNO_3 \cdot 2HC10_4$. The ionic constitution of this salt for many years was represented as follows: $(H_3NO_3)^{++}$ ($C10_4$)₂. Recently, however, Rousselet (ref. 24) was able to show that this material can be formed by the solid state reaction between hydronium and nitronium perchlorate salts:

$$H_{3}O^{+}C10_{4}^{-} + NO_{2}^{+}C10_{4}^{-} \longrightarrow (H_{3}O^{+}) + (NO_{2}^{+}) + (C10_{4}^{-})_{2}$$
(1)

By careful infrared spectroscopic work, Hantzsch proved that the product (1) was indeed a mixed perchlorate salt containing (H_3O^+) and (NO_2^+) ions. The remarkable part about this discovery is that (H_3O^+) and (NO_2^+) are compatible in the same crystal lattice, which is a fairly stable solid solution. Nitronium perchlorate is well known for its extreme tendency to decompose rapidly and become shock sensitive in the presence of moisture. Also, of interest, H_3OC10_4 forms orthorhombic crystals, whereas NO_2C10_4 is monoclinic. This illustrates that the components of solid solutions do not necessarily have to be isomorphous. Other examples of inorganic, high energy solid solutions are known. Hirsch (ref. 9) investigated the solid solution system formed between CsC10₄ and NH₄C10₄. Both crystals are orthorhombic. Hirsch found that this system belongs to Roozeboom's Type 1 (ref. 23). He concluded that the nonideal behavior in the system was due to the significant difference in size of the cations: $Cs^+ = 1.15$, $NH_4^+ = 1.43A$.

Deb (ref. 3) actually demonstrated how the properties of an inorganic explosive crystal could be improved by formation of a solid solution. He observed that T1N₃ and T1₂CN₂ tend to crystallize under the same conditions. Taking advantage of this fact, he impregnated T1N, with T1, CN, by a cocrystallization process. However, in the fresh precipitate, the T12CN2 was concentrated in localized orange spots. A physical mixture had evidently been formed instead of a solid solution. When Deb heated the precipitate, however, the colored patches diffused into the bulk of the crystal so that the crystal became uniformly light yellow in color. The melting point of the solid solution T1N₃, containing about 7% T1₂CN₂, was 24° lower than that of the pure material. Effects of this treatment on three other properties were noted: the photoconductivity was lowered, sensitivity to photolysis was increased, and the sensitivity to thermally induced detonation was tremendously lowered. Russian investigators have also carried out work in explosive solid solution systems as evidenced by the paper of Karnaukhov and Druzhinin (ref. 10). They studied the ternary system of NaC104 - AP -H₂O at 25° and reported that solid solutions were formed. Both of the abovementioned component salts belong to the orthorhombic crystal system. In a later paper Karnauknov (ref. 11) reported on the study of the AP-AN and

 $NaC10_4$ - $NaNO_3$ system and the ternary mixtures thereof. ARRADCOM recently compiled a number of translations of Russian papers dealing with phase relationships between an inorganic salt pair in water where solid solutions might be formed (ref. 26).

Although a considerable number of cases of cubic solid solutions have been identified, the number in other crystal systems is much less. This is no doubt due, at least in part, to the tremendously increased complexity of studying cases where the symmetry is lower. In many instances where an investigator may have been working with a system that formed a complex solid solution, he might not have been aware of or have been able to prove that this was the case. In spite of the difficulties involved, some excellent work has been done in studying solid solutions in noncubic systems. Hill (ref. 8) was a leading investigator in this field, who for many years studied phase systems formed from isomorphous salts in aqueous solution. He worked with the monoclinic, hexahydrated double sulfates of univalent and divalent bases, such as Mohr salt, Fe(NH4)2 (SO4)2.6H2O. These salts are also known as picromerites. Study of structural relationships in isomorphous series of alums, such as NH4 Ga (SO4) 2.12H2O, KGa (SO4) 2.12H2O, etc., was pioneered by Klug (ref. 13 and 14), who studied the change in lattice constants as a function of composition.

Of course, many other examples of studies of inorganic or metallic solid solution systems exist. The unique electrical properties of modern semiconductor materials are dependent upon the effect of adding trace impurities to highly pure metal or intermetallic crystals. Many modern alloys and ceramic materials are systems of solid solutions. They occur in nature in the form of minerals the composition of which, for instance, can vary with one ion being replaceable by another ion of similar radius and electrovalency.

With these data as a technical basis this program was initiated in an effort to make new oxidizer solid solutions "alloys." This report is an account of the findings as a result of this work.

PROCEDURES

Experimental Procedures

Crystal Synthesis

Isothermal Evaporation. This procedure has been described by Glasstone (ref. 6). Small amounts of the following solid solutions were made at the start of the program:

- AP-KP
 AP-KMnO₄
 KP-KMnO₄
- 4. AP-KP-KMnO

Varied, relative quantities of saturated solutions of the three salts in water were poured into Petri dishes and mixed. Then, the combined solutions were allowed to evaporate to dryness at ambient temperature.

Isothermal Cocrystallization. Samples of solid solutions for characterization studies were obtained by this method. The following systems were used:

- 1. AP-KP-H₂O at 25.0°C.
- 2. AP-AN-H2O at 25.0°C.
- 3. AP-KN-H₂O at 25.0°C.

In the first system, the phase data of Karnaukhov (ref. 12) and, Simanova and Shults (ref. 25) were available for making the synthesis calculations. Data were selected from the latter two investigators as being more accurate and were utilized instead of those data from Karnaukhov. In system 2, a different set of Karnaukhov's data (ref. 12) was relied upon for this work. The same investigator's data (ref. 12) were also used for system 3.

The first step in utilizing the published phase data to prepare a solid solution with a given target composition was to construct a ternary Gibbs' plot with concentrations expressed in percentage by weight. The latter units were the easiest ones to use for our purposes. A large triangular coordinate grid paper was used for this purpose.

In the AP-KP-H₂O ternary system a series of materials were prepared, the target compositions of which ranged from 5% AP-95% KP to 95% AP-5% KP. In instances where experimental tie lines (fig. 1) did not exist for the exact composition desired (table 1) hypothetical tie lines were established by inspection. This was graphically done by relying on the relatively large number of experimentally determined tie lines and on the high degree of symmetry of the Gibbs' plot in question (fig. 1). In the other two systems, however, in certain critical parts of the Gibbs' plots (figs. 2 and 3) the tie lines were fewer in number and were distributed in a less regular manner. Consequently, another method of constructing a hypothetical tie line (as seen in fig. 4) would terminate at a particular, desired solid solution of Composition A, situated on the dry solid phase line EF.

The latter procedure involved plotting a graph (fig. 5) representing the variation of the concentration of all three components of the system on the solubility curve, HK, (fig. 4) as a function of the concentration of one of the two salts in the solid solution phase along line EF. Coordinates of points for the dependent variables were taken at the terminus D of an experimentally determined tie line AD on the solubility curve HK.

This procedure was used as the basis for synthesis of AP-AN solid solutions. In the AN-KN types the existing tie lines available from Karnaukhov's original data were relied upon. After a tie line had been selected and established for an experiment, a particular point such as B or C (fig. 4) had to be located to serve as the initial experimental system. The concentrations of the three components corresponding to this selected point were used to make up the initial synthesis system. This point was selected so that a reasonable quantitative balance would be maintained between liquid and solid phases after chemical equilibrium had been established. The required amounts of both salts and water were weighed into the container used for the experiment. When glass tubes were used to prepare the AP-KP solid solutions, the necessary amount of AP and water were first mixed. Then the weighed amount of KP was added. When KP was added first, some difficulty arose in that caking of the salt mixture.

A variety of containers were tried during the course of this work. As far as glass tubes were concerned, the preferred method was to put several 0.79 cm diameter stainless steel balls in a "necked-down" glass tube. After the tube had been loaded with the salts and water, it was carefully sealed in stages with a glassblower's torch to protect it from too much heat. This tube was inserted in a larger tube with standard taper glass joints. The ends were cushioned with glass wool so the inner tube would not break upon rocking or inverting. The system was placed in a rocking or rotating device in the bath maintained electrically at 25.0°C. Agitation to provide grinding by sloshing of steel balls, salt, and water was achieved by means of a motor-driven system. Upon termination of the experiment, samples of equilibrium liquor were removed for analysis, and the solid salt phase was separated from the liquid as quickly and as thoroughly as possible. This was done on a fritted glass filter funnel which was attached to a water aspirator system. Some of the salts were dried further by placing them on absorbent fluorocarbor material or by pressing them between ordinary filter paper. The salts were subsequently dried in a vacuum oven at ambient temperature, or, in the case of AP-KP solid solutions after initial drying at ambient temperature then again at about 40°C for several hours until constant weight was attained. They were pulverized with a mortar and pestle and separated into different fractions according to particle size by passing them through standard screens.

An alternate procedure was used to make larger quantities of products. This involved weighing the salts and water in a glass mortar and pestle, which was then double-sealed in plastic bags. The system, from which no water vapor could escape, was placed in a weighted, transparent plastic Nalgene can. This was immersed in the water bath at 25.0°C. Several times a day the mortar and pestle in the plastic bags were removed and the system was ground by hand for about 5 minutes. Care was taken to keep the surroundings at nearly 25.0°C during grinding. During some experiments, tiny amounts of solid were removed from the system and analyzed by DTA. This was done in an attempt to determine whether equilibrium had been attained in the solid phase. The assumption was made that if DTA patterns of salts removed at sufficiently different times were identical, then the whole system was likely to be at equilibrium.

In one series of experiments three different solid solutions with different target ratios of AP-AN were synthesized concurrently. Three different glass mortar and pestles were used. All three systems were treated alike and handled together to eliminate or at least minimize the effect of transient environmental variables during the period of growth of the solid phase. Another feature of this set of three experiments, shown in table 2, was that extra pains were taken to provide as complete grinding as possible. This was done manually at near 25.0°C and was more frequent and thorough than in other experiments. Results of this work in synthesizing the three series of solid solutions are summarized in tables 1, 2, and 3.

Thermal Fusion. In the case of AN, which has a melting point of 169.9°C, AN could be used to melt and to dissolve other oxidizers. Solid solutions made in this way were as follows:

- 1. AN-AP
- 2. AN-KP
- 3. AN-TEPAN

Nearly all work was done on the microscale with a polarizing microscope equipped with a Koffler hot stage. Some mixtures were made up by weighing each ingredient. The mixture was placed on a glass slide and a cover glass was installed. During heating the component with the higher vapor pressure tended to sublime onto the relatively cooler cover glass. This of course caused the mixture remaining on the slide to be depleted with respect to the nonvolatile constituent. Some mixtures on the microscope slide were heated over an open flame. This permitted much more rapid heating than was possible on the Koffler hot stage. Also, the slide could be cooled quickly by placing it on a cold surface after the fusion had been completed. Some experiments were made in which AN and another isomorphous salt were heated carefully in a small test tube over an open flame. The tendency of AN to sublime away during heating was minimized in this way.

Chemical Analysis

Liquid Phases

The concentration of NH_4^+ containing salts in the liquid phase was determined by the Kjeldhal procedure. Potassium bearing salts were determined by atomic absorption spectroscopy.

Solid Phases

Dry salts were analyzed by means of the Kjeldahl method to establish the content of NH_4^+ salts. In a few cases total chemical analysis was carried out. Schwarzkopf Microanalytical Laboratories, Woodside, New York, made analyses of the K⁺ and C10₄⁻ content of AP-KP mixed crystals. Crobaugh Analytical Laboratories, Cleveland, Ohio, carried out analyses of AP-AN mixed crystals for NO₃⁻ and C10₄⁻ content.

Analysis of solid solutions that had been pulverized and graded according to particle size was carried out to determine whether much variation occurred in composition of the different fractions. These analyses were of the Kjeldahl type of determining ammonia. In this way the amount of AP and AN could be determined directly, and the quantity of the second salt deduced by the difference.

DISCUSSION

Theoretical Considerations

This work was based on a new concept in oxidizer chemistry, which is: Isomorphous relationships and phase rule theory can be used to predict the formation of oxidizer solid solutions which can have unique and valuable properties. Their nature can be forecast to some extent if one considers the factors above in relation to physical, chemical, and explosive properties of the crystals.

The AP-KP Solid Solution System

The crystal data of Donnay and Nowacki (ref. 5) in tables 4 and 5 show why these components have a virtually ideal isomorphous relationship. Each has Pbnm symmetry, the same crystal type, and similar lattice constants. Only a 7.7% difference exists in the size of the NH_4^+ and K^+ ions. Further indication of the close isomorphous relationship is seen from the optical data of Porter and Spiller (ref. 19).

The data from an Army bulletin (ref. 1) in table 6, clearly show that KP is more stable thermally than AP and also less impact sensitive. Thus, incorporation of KP into AP's crystal lattice could be expected to stabilize it. Also one can predict from the data of Trona (ref. 28) in table 7 that KP solid solutions and AP should reduce the latter's sensitivity to moisture.

Ideality of the AP-KP-H₂O System at 25°C

Data of Simanova and Shults (ref. 25) were tested by phase rule methods to determine the Roozeboom classification and the degree of ideality of the behavior of AP and KP in water at 25.0°C. Both Blasdale (ref. 2) and Ricci (ref. 22) have described the Roozeboom classification of solid solutions. In addition to the latter's original five types Ricci added a sixth (ref. 20). We also reviewed the subject recently (ref. 17) giving particular consideration to the synthesis problem with relation to the degree of ideality of the system.

Ricci (ref. 21) described methods for theoretical treatment of phase rule data on solid solution systems based on thermodynamic principles. With the use of Simanova and Shults data tje relationship was obtained, shown in figure 6, that is characteristic of a Roozeboom Type I case. Also, R_1 and R_5 values were obtained that represent the mole ratios of the interchangeable ions in the liquid and solid phases, defined in the last-mentioned paper. In an ideal case the relationship between R_1 and R_2 is a linear one. As can be seen from figure 7, Ricci's alums, A-1 through A-4 (ref. 21), show this ideality over the range indicated. The ternary perchlorate solid solution system, S-1 with water as the solvent shows a slight deviation from ideality at the one extreme. This system, however, evidently affords a favorable prototype for studying by phase rule methods the formation and properties of a continuous series of heat sensitive solid solutions.

The AP-AN Solid Solution System

Considerations similar to those used to theoretically evaluate the AP-KP system indicated that AP and AN should also form solid solutions. Karnaukhov's data (ref. 12) on the AP-AN-H₂O system at 25.0°C confirmed this.

Crystal data for AP and AN (ref. 4) clearly show that insofar as the "normal" orthorhombic forms are concerned, the two crystals are related isomorphically. Their lattice constants though are not so close as in the case of AP and KP. This could have a definite bearing on their capacity to form solid solutions (ref. 16). In addition to the similarity between these forms both species revert to structures of higher symmetry, namely cubic, at elevated temperatures. These respective cubic forms probably have some mutual solubility. One can conclude that the two salts might tend to form solid solutions by precipitation from water in the presence of one another. These observations have been experimentally verified by Karnaukhov (ref. 12) who asserted that "the investigated salts are isomorphous and form continuous solid solutions at any ratios."

The explosive parameters of AP and AN taken from an Army bulletin (ref. 27) and our own tests are shown in table 8. These tests showed that AP has a higher explosion temperature at the 5-second point than does AN. It is also much less sensitive to moisture than the latter salt. AN has an additional unfavorable property in that it undergoes five structural changes with appreciable accompanying variations in density over a range of less than 200°C. This causes problems in maintaining the mechanical integrity of the propellant grain. Such propellants also tend to be difficult to ignite and to burn slowly.

Ideality of the AP-AN-H₂O System at 25°C

When Karnaukhov's data on this ternary system were examined by the methods described above, the solubility relationship (shown in fig. 8) was suggestive of a Roozeboom Type IV case. From the data available, a horizontal portion in the curve (shown by the dotted line) cannot be determined as is found in the Type IV systems. However, a discontinuity is evident in the series of solid solutions and the two different types may be present. The irregular curve, K-1 (fig. 7) is a further indication of the lack of ideality of the behavior of this pair of salts in water at 25.0° C.

One of the most important aspects of replacement of other inorganic oxidizers, such as in solid solutions by AN, is its very low cost. It is one of, if not the cheapest, energetic chemicals available and is produced in massive quantities by many different manufacturers all over the world.

The AN-KN Solid Solution System

The ternary system of this isomorphous salt pair of AN and KN in water at 25.0°C was studied by Karnaukhov (ref. 12). The Gibbs' plot representative of the system is shown in figure 3. This system differs from the previous two in that an additional compound, 3KN·AN, is formed. According to data presented in figure 9, the system from the point of view of a Roozeboom classification is a considerably less ideal one than that of AP-KP-H₂O. A comparison of some chemical and explosive properties of the two oxidizers is shown in table 9.

AN is evidently a more energetic material than KN. Thus, AN should have the capability of upgrading KN with respect to energy in solid solutions. At the same time, KN is more stable and is less moisture sensitive than AN and, thus, might be expected to improve upon the deficient characteristics of the latter in isomorphous combinations.

The AN-KP Solid Solution System

This combination is theoretically attractive because of the vastly greater stability and moisture resistant characteristics of KP. In isomorphous solid solution combination with AN the indicated improvements should be obtained. Karnaukhov (ref. 12) studied the quaternary mutual system formed by these two salts in water at 25°C:

KC104 + NH4 NO3 ____ NH4C104 + KNO3

In this system, the double salt, 3KN•AN, is formed. The following solid solutions are obtained from the system:

3KN•AN-KN 3KN•AN-KP 3KN•AN-AN 3KN•AN-AP AP-KP Thus, the four component salts and the double salt must be related isomorphously. Unfortunately, the desired solid solution combination, AN-KP, does not appear in the system and, therefore, cannot be made in this way.

The AN-TEPAN or PEHAN Solid Solution System

TEPAN has been of interest for use in gun propellant formulations. Both it and PEHAN are chemically rather ill-defined, poorly-crystalline materials, which are difficult to characterize. The chemical formulae are represented in a somewhat approximate manner as follows:

TEPAN

PEHAN

TEPAN has a high gas volume and relatively low energy. When used in place of nitroguanidine in the M30 gun propellant formulation, it has exhibited a slightly higher force and lower flame temperature than the standard one. Also, it possesses superior physical properties when compared to a nitroguanidine composite and is inexpensive. In view of the fact that AN has a relatively high oxygen content and energy, this might be expected to form solid solutions with TEPAN or PEHAN that would give even greater force in gun propellants. Of course, AN is an eminently inexpensive chemical and, as mentioned previously, nearly always has the capability of lowering the cost when used to replace other oxidizers.

Ternary Solid Solution Systems with KMnO, Component

Inclusion of small amounts of KMnO₄ in oxidizer solid solutions is of some potential interest from a catalytic point of view. Manganese dioxide is commonly used as a decomposition catalyst for potassium chlorate. A similar catalytic effect might possibly result with KMnO₄ in intimate combination with other materials containing high oxygen contents. Thus, the presence of permanganate could promote higher burning rates in composite propellants. Potassium permanganate is isomorphous with AP and KP and thus should readily form solid solutions with either one.

Crystal Synthesis

Isothermal Evaporation

This procedure was abandoned in the early stages of our work inasmuch as the product is a mixture of solid solutions having different compositions. Ternary types composed of AP-KP-KMnO₄ were made and characterized briefly. Our aim was to make as nearly as possible completely homogeneous materials that would lend themselves to serious characterization studies and that could be made in virtually identical lots upon repeated synthesis.

Isothermal Cocrystallization

This method was used to prepare solid solutions for extensive characterization studies. The method proved to be capable of giving a product that, for all practical purposes, is homogeneous (ref. 18). At the same time if one departed from the techniques used in rigorous phase rule studies the problem of attainment of true chemical equilibrium could arise. The development of a simple method requiring no elaborate apparatus for making larger batches of the solid solutions on a lab scale was of particular concern. With glass tube containers product quantity was 10-20 grams. Much more than this was needed for AP-KP burning rate studies, for instance. To try to substantially increase the size of the glass tubes was impractical. For this reason glass mortars and pestles were resorted to for the experiments. In one case about 100 grams of the AP-KP type were made in a single experiment. The AP-KP solid solutions made by the mortar and pestle techniques were fairly uniform in composition as illustrated in table 10. In both samples shown in this table, not much difference occurred in the compositions of large and small particle size fractions obtained by grinding and sieving. This work served to establish that, under optimum conditions, the mortar and pestle technique could be used satisfactorily to obtain solid solutions that in a practical sense are homogeneous.

The problem of attainment of chemical equilibrium and homogeneity in the solid solution phase in the AP-AN-H₂O system proved to be difficult. In the first place to obtain increased amounts of product for characterization studies a higher relative amount of salt with respect to water than with the AP-KP-H₂O system was required. In the latter case (table 1), 50% water was used; whereas, with the former (table 2), 20-31%

was employed. All experiments in the AP-AN-H2O system were made with the mortar and pestle technique. From the data shown in table 11 the particular conditions of each experiment were critical insofar as attainment of solid solution homogeneity was concerned. Experiments 2 and 5 were made in a manner similar to that used for the AP-KP types of table 10. Results in experiment 2, in particular, showed that the outer and inner parts of the crystals differed considerably in composition. In view of this problem a set of three simultaneous experiments was devised to determine whether more thorough grinding would give better results. These were 1, 3, and 4, table 11. They were carried out at the same time in as nearly alike manner as possible. In this way the expectation was that variables such as temperature, stirring efficiency, etc., would be eliminated from consideration. Experiment 4, in this new series, gave much better results than the earlier one, number 2, where less efficient grinding was used. Actually, the product of experiment 3 was more homogeneous than might appear at first glance from the data in table 11. The unground material and particles of sizes < 210 > 44 microns were similar and not far from the 1:1 target composition ratio. The < 44 micron size material on a weight basis represented only a minor part of the solid solutions. Insofar as attainment of a homogeneous product is concerned, conditions used in this set of three experiments (1, 3, and 4) were apparently fairly satisfactory. Even in this more difficult synthetic case of the AP-AN-H2O system, with proper care, the simple mortar and pestle technique can evidently be used satisfactorily. It was impossible to establish without further experimentation whether variations in target and actual compositions of the crystals might have been due to errors in Karnaukhov's data on this system.

The AN-KN-H₂O system represents a thermodynamically less ideal case than does the AP-AN-H₂O one, as indicated in figure 9. In spite of this materials were prepared that apparently are a little more homogeneous, table 12, than those with the latter system, table 11. An unusual feature of this system is that a double salt 3KN-AN is obtained that forms two series of solid solutions with the respective KN and AN components. Experiment 2 gave the best double salt product. The large particles < 420 > 250 microns differed in AN content only by 2.22% from theoretical for the double salt. Questions arose as to whether errors might exist in Karnaukhov's original data on this system. Another of Karnaukhov's papers was found to contain defects as pointed out by fellow Russian workers (ref. 25). Most commonly, the cause of errors in such work is failure to attain complete chemical equilibrium. Again, accurate judgment was not possible in the absence of much more experimentation.

Thermal Fusion

The chief significance of our brief efforts in this area was that we found that solid solutions composed of AN and KP could apparently be made in this way. As pointed out previously the isothermal cocrystallization process cannot be used to obtain solid solutions of this salt pair. Instead, a sample composed of three parts AN and one KP by weight was heated to the point of fusion, which showed a different X-ray diffraction pattern when cooled and solidified than the components or the original unheated mixture. In other respects the sample was incompletely characterized. Experiments in making solid solutions of AN and TEPAN were also essentially preliminary.

Chemical Analysis

Liquid Phases

The analytical work with equilibrium liquid phases from the AP-KP-H₂O system confirmed the solubility curve of Simanova and Shults, figure 10. In the AP-AN-H₂O and AN-KP-H₂O systems, on the other hand, no attempt was made to experimentally establish the solubility curve for the respective salt pairs. Thus, as pointed out previously, to determine whether Karnaukhov's data (ref. 12) on these phase diagrams are completely correct was not possible within the scope of this study.

Solid Phases

Not only the gross composition of our solid solutions was established by chemical analysis but, as shown previously, also evaluated the degree of homogenity therein. Compositions of different particle size fractions of the same product of pulverized material (as shown in tables 10, 11, and 12) were compared, and the effectiveness of the synthesis efforts was judged in the attainment of true equilibrium conditions. It is noteworthy that a small amount of nonequilibrium solid solution is unavoidably included in the solid phase. This is a result because, in a practical sense, neat recovery of a solid phase from a liquid phase is impossible. No matter how carefully this is done, a small amount of liquid phase adheres to the solid phase. The water in the solution evaporates and a small amount of crystalline matter is deposited by an essentially isothermal evaporation process. Thus, when the crystals are pulverized and graded by screening, the finer sized fractions (outer coats), i.e., $< 44\mu$, expectedly differ substantially in composition from the cores of the crystals as represented by the analyses of the larger particle size fractions. The "fines," in general, represent a relatively small (i.e., 5-10) percent of the solid solutions on a weight basis.

CONCLUSIONS

The new approach used in this work for the development of unique solid solution oxidizers is judged to be successful. Consequently, it constitutes an important contribution toward the advancement of the art of solid propellant rocketry. Concepts of isomorphism and phase rule chemistry can be used to select and prepare oxidizer materials of theoretical interest. Model solid solution systems show results consistent with theory.

Though definite limitations exist in the practical application of concepts explained here, significant opportunity for further growth is present. It is anticipated that future research in this area will result in additional advances.

RECOMMENDATIONS

The principles upon which this work is based have been shown to be valid. This program has not exhausted all of the possibilities in the oxidizer field, to say nothing of inorganic chemistry in general. Unfortunately, in the area of explosives continued exploration of solid solutions leads to investigations where exceptional experimental difficulties are likely to be encountered. However, where it has been shown that further progress is theoretically possible, such factors have not been a complete bar to progress. Consequently, similar research not only in the oxidizer field but also in a larger chemical sense should be encouraged and supported.

REFERENCES

- 1. Anon., AMC Pamphlet 706-187, Engineering Design Handbook, Military Pyrotechnic Series, Part III, Properties of Materials Used in Pyrotechnic Compositions, USAMC, October 1963.
- Blasdale, W. C., Equilibria in Saturated Salt Solutions, Chemical Catalog Co., Inc., NY 1927.
- Deb, S. K. et al., 8th Symp. (Int.) Comb., Pasadena, CA, Sept 3, 1960, Pub. 1962, pp 829-36.
- Donnay, J. D. H., Donnay, G., Cox, W. G., Kennard, O., and King, M. V., Crystal Data Determinative Tables, Second Edition, Williams and Heintz Map Corp, Washington, DC 1963.
- Donnay, J. D. H. and Nowacki, W., Crystal Data, The Geological Society of America, Memoir 60, 1954.
- Glasstone, S., Textbook of Physical Chemistry, Second Edition, D. Van Nostrand Co., Inc., New York 1946, pp 806.
- 7. Hantzsch, Ber., 61, 1328 (1928); ibid, 61, (1928), p 1328.
- Hill, A. E. et al., J. Amer. Chem. Soc., 63, 1031-6 (1940); also other papers in this series.
- 9. Hirsch, Th.v., Zeit fuer Physik. Chem., New Series, 35, 24-46 (1962).
- 10. Karnaukhov, A. S. and Druzhinin, I. G., Doklady Akad Nauk. SSSR 84, 963-6 (1952); and also other papers.
- 11. Karnaukhov, A. S. Izvest. Seklora Fiz. Khim, Anal. Inst. Obshchei Neorg. Khim. Akad. Nauk. SSSR, 25, 334-344 (1954).
- Karnaukhov, A. S. Zhurnal Neorganischeskoy Khimii, II No. 4, 915-927 (1957).
- Klug, H. P. and Alexander, L., J. Amer. Chem. Soc., 62, 2993-5 (1940).
- 14. Klug, H. P. and Kieffer, G. L., ibid, 65, 2071-2 (1943).

15. McCrone, W. C., U.S. 3,147,160 Sept 1, 1964.

16. Morrow, S. I., J. Chem. Ed., 46, 580 (1969).

- Morrow, S. I., "Problems in Synthesis of Mixed Crystals," 24th Annual Northwest Regional ACS Meeting, Univ. of Utah, Salt Lake City, Utah, June 13, 1969.
- 18. Morrow, S. I. and Bracuti, A., Thermochim. Acta. 1 (1970), 317-324.
- 19. Porter, M. W. and Spiller, R. C., Barker Index of Crystals, Vol I, Part 2, Heffer and Sons Ltd., 1951.
- 20. Ricci, J. E., J. Amer. Chem. Soc., 57, 805 (1935)
- 21. Ibid, 62, 2723 (1940).
- 22. Ricci, J. E., "The Phase Rule and Heterogeneous Equilibrium," Dover Publications Inc., NY, 1966.
- 23. Roozeboom, H. W. B., Z. Physik. Chem., 8, 504 (1891).
- 24. Rousselet, D., Compt. Rend., 261, 23, Group 8, 5121-3 (1965); Ibid, November 29, 1965.
- Simanova, S. A. and Shults, M. M., Zhurnal Neorganischeskoy Khimii, 12, No. 1,223-230 (1967).
- "Solubility Diagrams of Various Ternary Systems, Two Inorganic Salts in Water," Technical Translation 70, Picatinny Arsenal, Dover, NJ, December 1967; Translations of Articles from Russian Journals.
- 27. Smith, S. D., Engineering Design Handbook, AMCP 706-177, USAMC, March 1967.
- 28. Trona Bulletin No. TD-7, Perchlorate Moisture Content, American Potash and Cehmical Corporation, Los Angeles, CA.
- 29. Wells, A. F., "Structural Inorganic Chemistry," 3rd Ed., Oxford at the Claredon Press, 1962, pp 185.
- 30. Ibid, pp 168.

Synthesis of AP-KP solid solutions

Expt.	ò	Comp	osition of re, § by	initial weight	solid target ci 8 by 1	solution omposition, weight	Solid s actual co & by w	olution mposition, eight	Differ actual v compos	ence, s target ition %
		4I	쥥	H ₁ O	٩I		٩I	₽I	٩I	βI
6-d	-	48.10	1.89	50.01	95.0	5.0	94.81	5.19	-0.19	+0.19
P-10	7	46.25	3.75	49.99	90.0	10.0	89.70	10.30	-0.30	+0.30
P-11	m	44.14	5.75	50.12	85.0	15.0	83.76	16.24	-1.24	+1.24
P-12	4	42.10	7.89	50.01	80.0	20.0	79.41	20.59	-0.59	+0.59
P-8	•	39.99	9.98	50.02	75.0	25.0	74.20	25.80	-0.80	+0.80
P-15	9	36.57	13.40	50.01	66.4	33.6	65.13	34.87	-1.27	+1.27
P-7	1	29.47	20.47	50.05	50.0	50.0	51.23	48.77	+1.23	-1.23
P-2	80	29.50	20.50	50.00	50.0	50.0	50.23	49.77	+0.23	-0.23
P-16	6	23.90	26.20	49.90	37.0	63.0	36.74	63.26	-0.26	+0.26
9-d	10	17.60	32.43	49.97	25.0	75.0	25.87	74.13	+0.87	-0.87
P-14	=	8.19	41.74	50.07	9.0	91.0	7.12	92.88	-1.88	+1.88
P-13	12	2.61	47.35	50.03	5.0	95.0	1.44	98.56	-3.56	+3.56

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Synthesis of AP-AN solid solutions

Expt. N	ė	Comp	osition of ire, § by	initial weight	Solid s target co § by w	olution mposition, eight	Solid so actual con 8 by we	olution nposition, eight	Differe actual vi compos	ence, s target ition %
		٩	쥥	0 ⁴ H	٩		٩I		٩	٩
APN	-	40.0	40.0	20.0	75.0	25.0	97.5	2.5	+22.5	-22.5
APN c	~	31.0	43.9	25.2	75.0	25.0	87.0	13.0	+12.0	-12.0
AI- MP-1	m	17.64	51.41	30.95	75.0	25.0	84.28 ^a	13.89 ^a	+ 9.28	- 9.28
APN	4	22.60	57.40	20.00	50.0	50.0	31.0 ^b	9.0 ^b	-19.0	+19.0
APN c	Ś	15.60	59.30	25.00	50.0	50.0	53.9	46.1	+ 3.9	- 3.9
APN 1 (4)	ø	6.55	67.90	25.60	25.0	75.0	7.3	92.7	-17.7	+17.7

^aComposition determined by total analysis by Crobaugh Analytical Laboratories, Cleveland, Ohio.

 $^{\rm b}$ Product was pulverized and separated into fractions of different particle sizes. The fraction analyzed here was that of larger ones, namely $>149\mu$.

^CThese experiments were run in same way at the same time.

Synthesis of solid solutions and an addition compound from AN and KN

Expt.	No.	Com	position of ure, % by	initial weight	Solid s target co % by v	solution mposition, veiaht	Solid so actual cor & bv w	olution nposition, eiaht	Differ actual v compos	ence, 's target ittion %
100		 ₹	₽I	윜	el el		- del	₽	4	₽
KN- AN-2	-	61.0	19.0	20.0	75.0	25.0	68.72 ^a	31.28	-6.28	+6.28
KN- AN-1	2	35.0	45.0	20.0	20.5	79.5	22.72 ^b	77.28	+2.72	-2.72
Addn. KN- AN-4	. Com	pd. 43.0	27.0	30.0	20.5	79.5	12.57 ^a	87.43	-7.93	+7.93
KN- AN-3	4	19.0	56.0	25.0	7.5	92.5	4.77 ^b	95.23	-2.73	+2.73

^a Material was ground and separated into different particle size fractions. This one was < 250 > 177 μ , a relatively large particle size.

^bThis was the largest particle size fraction of the crushed product, namely < 420 > 250µ.

Crystal data for orthorhombic forms

	_a/b	b	<u>a</u>	_ <u>b</u>	_ <u>c</u>
NH4C104	0.8048,	0.6291,	7.42,	9.22,	5.80,
	0.8095	0.6320	7.449	9.202	5.816
KC104	0.8181,	0.6395,	7.24,	8.85,	5.66,
	0.8193	0.6396	7.240	8.8373	5.65212

Table 5

Crystal data for cubic forms

		a
NH ₄ C10	(at 270°C)	7.65
	(at 243°C)	7.69
KC104	(at 340°C)	7.49
	(at 310°C)	7.52

Each has Pbnm symmetry, the same crystal type, and similar lattice constants. There is only a 7.7% difference in the size of the NH_4 and K^+ ions. Further indication of the close isomorphous relationship is seen from the optical data.

5

Explosive parameters of perchlorates

Property or test	<u>AP</u>	KP
Impact sensitivity, 2 Kg wt Picatinny, In.	24	40+
Heat of formation K cal/mole at 298°K	-69.42	-103.6
Decomposition Temperature, °C	begins at 130, becomes explo- sive at 380	starts about 530
Melting point, ℃	decomposes about 150	610±10

Table 7

Perchlorate moisture sensitivity

Property or test	AP	KP
Critical relative humidity, % at temp. ℃	94.5 at 22.5°	99.4 at 21.1°
Equilibrium moisture content, % H ₂ O (% of dry weight) at percent relative	1.19 at 100% R.H.	0.116 at 100% R.H.

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Oxidizer explosive properties

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Property or test	AP	AN
Impact sensitivity	21	40+
2 Kg wt, in. Picatinny test ¹	(18)	(15)
Explosion temperature, °C, 5 sec point ³	403	232
100°C heat test, % loss 1st 48 hours	0.02	0.74
Structural transition	240	-60, -18,
temperatures, °C		32, 84, 125
Melting point, °C	dec.	169.9

¹This value is from our tests with material of particle size < 149 > 74 microns. Figures below in brackets are sample weights in gm.

²This is our value with particle sizes given in footnote 1.

Oxidizer explosive properties

Property	AN	KN
Oxygen, %	60	47.48
Density, gm/cm	1.725	2.109
Coefficient of thermal expansion 0-100°C	982 to 1113 × 10 ⁻⁶	196.7 × 10 ⁻⁶
Free energy of formation K cal/mole at 298°K	n, -43.82	-93.96
Melting point, °C	169.7	338
Heat of fusion, K cal/mole	1.3 to 1.53	2.8
Boiling point, °C	dec. 210	400
Transition point, °C		
Form V Form IV Form III Form II Form I	-18 32.2 84.2 125.2	α 128 β
Hygroscopicity 65% R.H., gain		
mg/g 24 hrs.	131.6	< 1

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Homogeneity of experimental AP-KP solid solutions

	Sample No.	Particle size, microns*	Target AP content, % <u>by weight</u>	content, % by weight <u>by analysis</u>	Difference <u>§ by weight</u>
P7A2A	-	<210> 177 <44	50.0 50.0	49.32	2.31
P12(A)	7	unground <210> 44 <44	80.0 80.0 40.0	80.02 80.99 76.69	- 4.30

*The product was pulverized and graded according to particle size by screening.

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Homogeneity of experimental AP-AN solid solutions

APN 1(4)	Experiment number ¹	Particle size, microns ¹ unground	Target AP content, % <u>by weight</u> 25.0	Actual AP content <u>§ by weight</u> 7.3	Difference, 8 by weight
		<210>44 <44		6.6 11.1	4.5
	7	>149 <44	0.6/	31.0 85.7	
II NAK (h)	m	unground <210>44 <44	50.0	53.9 49.0 74.5	
(h)	ŧ	unground <210>44 <44	75.0	87.0 87.0 83.8	3.2
APN III	'n	>149 <44	75.0	97.5 89.5	

Experiments 1, 2, 3, 4, and 5 correspond to numbers 6, 5, 4, 2, and 1 respectively of table 2.

³The product was pulverized and separated into different particle size fractions by screening except in cases where it is specified as being unground.

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Homogeneity of products obtained from the AN-KN-H₂O system at 25.0°C

	Experiment number	Target composition, § AN by weight	Actual composition, 8 AN by weight	Particle size of material	Difference between extremes, §
KN-AN-2	-	75.0	68.72 68.50 68.34	<250>177 <149>74 <44	0.38
KN-AN-1	2	20.5	22.72 16.48* 27.43	<420>250 <149>74 <44	4.71
tr-NA-4	m	20.5	12.57 10.83 15.37	<250>177 <149>74 <44	2.80
KN-AN-3	4	7.5	4.77 5.52 11.30	<4420>250 <149>174 <444	6.53

*This analytical result is rather unexpected and leads on to question whether or not it might be in error.













Variation of coordinates on solubility curve with relation to AN in the solid phase

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Figure 7. Salt distribution in AP-KP-H₂O, and AP-AN-H₂O systems compared to those in ideal alum systems









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INVESTIGATION OF PROPELLANT AND EXPLOSIVE SOLID SOLUTION SYSTEMS: I. CRYSTAL SYNTHESIS

Scott I. Morrow Nathaniel S. Gelber Roscoe Croom

May 1978

A chemical group was omitted from the formula for PEHAN on page 11. The formula should be as follows:



	H	H		H	H	H	H		H	H		H	H	
NH3-	ċ.	-ċ.	-NH2	-ċ.	-C-NH2	-Ċ	-Ċ	-NH2	-ċ	-Ċ	-NH2	-Ç.	-C·	-NH3
1	Ĥ	Ĥ		Ĥ	н.)	H	H	1	Ĥ	Ĥ	1	Ĥ	H	1
NO3			NO3		NO3			NO3			NO3			NO3

16 August 1978

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