

Dehydration of Hydrated Crystals by Boiling Nonaqueous Liquids*

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Many hydrated crystals can be caused to give up their water of crystallization at temperatures below those obtained when heated in air, if they are immersed in boiling, nonaqueous liquids.

There has been but little work reported upon this peculiar behavior of salts containing water of crystallization. Pritzker and Jungkunz (2) attempted to apply the method of Dean and Stark (1) to the analysis of hydrated blue vitriol and copperas, whereby they sought to determine the amount of water present in these hydrated salts. They found that copper sulfate yielded four of its five molecules of water of crystallization and hydrated ferric sulfate lost $6\text{H}_2\text{O}$, when heated in boiling xylene and that higher temperatures (200°C . and 300°C ., respectively) were required for their complete dehydration.

The amounts of water that can be removed from several hydrated salts have been determined, when a variety of water insoluble, organic liquids were used for distillation media.

Method Used for Obtaining Data

The apparatus consisted of the usual 500 c.c. short neck Pyrex flask, a 20-inch glass reflux condenser, a calibrated Bidwell-Sterling water receiver for liquids lighter than water and an A. S. T. M. distillation receiver (for crank case dilution) for liquids heavier than water. Ten grams of a hydrated salt were placed in the 500 c.c. flask, covered with 200 c.c. of liquid (benzene, xylene, etc.) and distilled in the prescribed manner (1). In general, distillation was continued either for three hours or until very little or no more water was collected in the receiver. Finally, the amount of water obtained in the receiver was read with all the precautions described in the author's previous (3) articles.

The use of liquids heavier than water is not recommended for an analytical method because it is more difficult to obtain accurate readings when two menisci are involved, which is the case when the recovered water floats on heavier-than-water liquid in the calibrated receiver.

Methylene chloride, boiling at 40.1°C ., must approach the lower limit of dehydrating temperature by a distilling liquid, because ethyl ether, boiling at 34.5°C ., is ineffective for dehydrating any crystal in this series, and in fact, it did not even entrain free water when placed in the distilling flask. This inability to dehydrate salts does not appear to have any bearing upon the composition of the liquid because another ether, isopropyl, will remove water from hydrated crystals under similar conditions. It boils at about 68.5°C .

Behavior of Hydrated Crystals

In some instances crystals gave up their water of crystallization at a fairly uniform rate throughout

the entire period of treatment. Therefore, the amount of water obtained varied directly with the time. Potassium alum behaved in this fashion, for when this salt was heated in the presence of distilling chloroform its composition indicated the formula, $\text{Al}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, at the end of three hours, and after four hours it contained only slightly less water than it did after three hours in boiling benzene.

Other crystals dehydrated with extreme ease, losing 100 per cent of their moisture at comparatively low temperatures. This type of crystal is illustrated by

sodium sulfate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$,
zinc acetate, $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$, and
sodium carbonate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$.

An interesting group of hydrated crystals are those that are not affected in the slightest way by lower boiling liquids, but which are completely dehydrated at a somewhat increased temperature. For example: potassium oxalate, $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, did not lose a trace of its water in the presence of boiling benzene, but it was practically completely dehydrated by boiling toluene in 30 minutes.

A fourth class of crystals are those that appear to form definite states of dehydration at different temperatures, between which no moisture whatever is lost, even during prolonged boiling. Copper Sulfate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, is a typical example, as it readily loses four molecules of water in the presence of boiling toluene, and the resulting product, $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, containing one molecule of water, is not affected by boiling xylene, but requires a much higher temperature (boiling tetralin) to cause it to lose the residual water.

A number of hydrated crystals were subjected to treatment with boiling, nonaqueous liquids, and these are recorded in the table below.

Calculation of Degree of Hydration of Treated Crystals

The amount of water collected was read as c.c.s and this value was calculated as molecules of water removed. The final hydrated state of the crystal that still contained moisture was then assumed to be the difference between the original amount of hydration and the amount of water obtained in the receiver.

These calculations generally did not produce whole numbers for the number of molecules of water retained. This was mainly due to dehydration becoming very slow towards the end of the indicated times, and therefore not becoming definitely completed. It was observed that some moisture, often only the faintest trace, could be continuously removed by prolonged distillation, after an apparent hydrated state was obtained.

A typical calculation of residual water of crystallization is illustrated by the dehydration of 10.0

* Because of the extensive data still to be obtained upon the subjects discussed in this paper, this presentation is offered as suggestion and guide for those who wish to do further research in this field.

DISTILLATION MEDIA

| Compound Tested | Methylene Chloride | | Chloroform | | Benzene | | Toluene | | Xylene | | Hi Flash Naphtha | | Tetraalin | |
|---|--------------------|---|------------------------|---|------------------------|--|------------------------|---|------------------------|--|----------------------|--|---------------------|-----------------|
| | a | b | a | b | a | b | a | b | a | b | a | b | a | b |
| Na_2CO_3 , 10H ₂ O | (w) 51.8% (t) 4 | Na_2CO_3 , 2H ₂ O | (w) 62.4% (t) 3 | Na_2CO_3 | (w) 63.8% (t) 3 | Na_2CO_3 ¹ | | | | | | | | |
| Na_3PO_4 , 12H ₂ O | (w) 28.1% (t) 4 | Na_3PO_4 , 3H ₂ O | (w) 47.4% (t) 3 | Na_3PO_4 | (w) 47.6% (t) 3 | Na_3PO_4 | | | (w) 47.9% (t) 2 | Na_3PO_4 | | | | |
| $\text{Na}_2\text{B}_4\text{O}_7$, 10H ₂ O | (w) 12.8% (t) 4 | $\text{Na}_2\text{B}_4\text{O}_7$, 7H ₂ O | (w) 26.2% (t) 4 | $\text{Na}_2\text{B}_4\text{O}_7$, 4 1/2 H ₂ O | (w) 24.6% (t) 1 1/2 | $\text{Na}_2\text{B}_4\text{O}_7$, 5H ₂ O | (w) 33.1% (t) 1 | $\text{Na}_2\text{B}_4\text{O}_7$, 2 1/2 H ₂ O | (w) 36.4% (t) 5 | $\text{Na}_2\text{B}_4\text{O}_7$, 2H ₂ O | | | | |
| Sodium Silicate 40% Sol. | | | | | (w) 56.8% (t) 3 | $\text{Na}_2\text{Si}_2\text{O}_6$, 1 1/2 H ₂ O | (w) 59.3% (t) 3 | $\text{Na}_2\text{Si}_2\text{O}_6$ | (w) 60.1% (t) 3 1/2 | $\text{Na}_2\text{Si}_2\text{O}_6$ ³ | | | | |
| Sodium ⁴ Meta- Silicate | | | | | | | (w) 24.9% (t) 3 1/2 | Na_2SiO_3 , 1/2 H ₂ O | | | | | | |
| Na_2SO_4 , 10H ₂ O | | | (w) 55.9% (t) 2 1/2 | Na_2SO_4 | (w) 55.9% (t) 2 | Na_2SO_4 | | | | | | | | |
| $\text{Na}_4\text{P}_2\text{O}_7$, 10H ₂ O | | | (w) 40.2% (t) 1 1/2 | $\text{Na}_4\text{P}_2\text{O}_7$ | | | (w) 40.3% (t) 1 1/2 | $\text{Na}_4\text{P}_2\text{O}_7$ ⁵ | | | | | | |
| Sodium ⁶ Acetate, +H ₂ O | | | | | (w) 50.0% (t) 3 | Anhydrous Salt | (w) 50.0% (t) 3 | Anhydrous Salt | | | | | | |
| Potassium Oxalate, 1H ₂ O | (w) 00.0% (t) 4 | $\text{K}_2\text{C}_2\text{O}_4$, 1H ₂ O | (w) 00.0% (t) 4 | $\text{K}_2\text{C}_2\text{O}_4$, 1H ₂ O | (w) 00.0% (t) 4 | $\text{K}_2\text{C}_2\text{O}_4$, 1H ₂ O | (w) 10.29% (t) 2 | $\text{K}_2\text{C}_2\text{O}_4$ ⁷ | | | | | | |
| $\text{K}_4\text{P}_2\text{O}_7$, +H ₂ O | | | | | | | (w) 50.0% (t) 2 1/2 | $\text{K}_4\text{P}_2\text{O}_7$ | | | | | | |
| Ca_3Cl_2 , +H ₂ O | | | | | | | (w) 8.4% (t) 4 | CaCl_2 | (w) 8.5% (t) 3 | CaCl_2 | (w) 8.65% (t) 3 | CaCl_2 | | |
| BaCl_2 , 2H ₂ O | | | | | (w) 14.7% (t) 1 | BaCl_2 | | | | | | | | |
| SrCl_2 , 6H ₂ O | | | | | (w) 40.5% (t) 4 | SrCl_2 | | | | | | | | |
| MgCl_2 , 6H ₂ O | | | | | (w) trace (t) 1 | MgCl_2 , 6H ₂ O | (w) trace (t) 1 | MgCl_2 , 6H ₂ O | (w) 45.2% (t) 4 | MgCl_2 , H ₂ O | (w) 53.5% (t) 1/2 | MgCl_2 ⁸ | | |
| Li_2SO_4 , 1H ₂ O | | | | | (w) 13.2% (t) 3 | Li_2SO_4 | (w) 13.2% (t) 3 | | | | | | | |
| CuSO_4 , 5H ₂ O | | | | | | | (w) 28.65% (t) 4 | CuSO_4 , 1H ₂ O | (w) 28.7% (t) 4 | CuSO_4 , 1H ₂ O | (w) 28.7% (t) 4 | CuSO_4 , 1H ₂ O | (w) 37.85% (t) 1 | CuSO_4 |
| Zinc Acetate, 2H ₂ O | | | (w) 16.9% (t) 4 | Anhydrous Salt | | | | | | | | | | |
| $\text{Al}_2(\text{SO}_4)_3$, K_2SO_4 , 24H ₂ O | (w) 14.6% (t) 4 | $\text{Al}_2(\text{SO}_4)_3$, K_2SO_4 , 16H ₂ O | (w) 29.6% (t) 4 | $\text{Al}_2(\text{SO}_4)_3$, K_2SO_4 , 8 1/2 H ₂ O | (w) 27.8% (t) 3 | $\text{Al}_2(\text{SO}_4)_3$, K_2SO_4 , 9H ₂ O | (w) 37.0% (t) 3 | $\text{Al}_2(\text{SO}_4)_3$, K_2SO_4 , 4 1/2 H ₂ O | (w) 38.9% (t) 3 1/2 | | | | | |
| H_3BO_3 | | | | | | | (w) 29.4% (t) 4 | HBO_3 | | | | | | |

¹ Original sample contained about 1.15% excess moisture by fusion test.

² Oven dried at 100° C., compound lost 47.68% of water. Upon fusion, it lost 47.93%. Original salt was partly dehydrated.

³ Separate sample fused in crucible lost 60.1% of H₂O.

⁴ The salt had partly effloresced. Upon fusion it lost 32.9% of H₂O.

⁵ The salt had slightly effloresced.

⁶ Ten grams of anhydrous salt plus 10 grams of water.

⁷ This salt was slightly wet in excess of water of hydration.

⁸ Barring the loss of HCl during dehydration, this indicates a better desiccant than CaCl₂.

grams of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (Borax) by means of methylene chloride. After four hours of distillation, 1.28 c.c. of water (equal to 12.8 per cent) was collected.

$$\text{Hence, } \frac{381.43 \text{ (mol. wt. of borax)} \times 0.128}{18} = 2.78,$$

assumed to be equivalent to 3 H_2O .

Then, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} - 3\text{H}_2\text{O} = \text{Na}_2\text{B}_4\text{O}_7 \cdot 7\text{H}_2\text{O}$ (final state).

All pertinent data are condensed in the following table, in which are columns "a" and "b." In the "a" columns are tabulated the per cent of water (w) obtained during each separate distillation, during the time (t) in hours, and in the "b" columns are given the approximate formulas of the corresponding compounds.

Deductions from Experimental Data

Since both time and speed of distillation have considerable bearing upon the amount of water removed from some crystals, it cannot be asserted that a defi-

nite state of partial dehydration can universally be obtained.

Besides revealing that salts can be prepared that at present appear to have unusual states of hydration, these data have analytical significance. For example, upon applying the distillation method for the determination of moisture in soaps and soap powders containing hydrated salts for fillers and builders, the analyst cannot always assume a completely dehydrated residue remains in the flask but he must take into account the actual salt present and the state of its dehydration in respect to the distillation medium. Also, another matter of analytical interest is that upon knowing the degree of dehydration obtainable with a selected distillation medium, it is possible to determine the original state of hydration of many normally hydrated crystals that have lost a portion of their water of crystallization through drying. The process has been shown to be applicable to salts of both inorganic and organic acids.

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Deterative Efficiency of Tetrasodium Pyrophosphate — Part II

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The tentative conclusions for Part I were that tetrasodium pyrophosphate possessed the following advantages:

- 1) Ability to increase suds.
- 2) Ability to increase detergency.
- 3) Ability to increase the amount of builder without diminishing the cleaning efficiency of the soap.
- 4) Low pH for use in household soaps.

It was indicated then, that final conclusions as to its value when combined with other builders would have to await completion of experiments with ternary combinations. It may be said at once that this work in no way alters the conclusions which were then drawn.

The purpose of this paper is four-fold:

- 1) To present concentration vs. efficiency curves for ternary combinations of alkaline builders.
- 2) To discuss more fully the wash test method and the accuracy of the data presented.
- 3) To suggest means for the practical utilization of the data.
- 4) To present a recapitulation of general conclusions.

* Deceased.

Concentration vs. Efficiency Curves for Ternary Combinations of Builders

Since results with binary mixtures of builders varied more or less directly with the proportions of the builders present in the combination (and their individual effectivenesses), it was decided that ternary combinations would be tested in a 1:1:1 ratio, thus reducing the specific effect of any one builder in the combination.

It became evident that the results with the ternary mixtures were indeed dependent upon the ratios of the builders present, hence the total number tested were limited. The individual builders in these combinations were chosen as representative of those finding greatest commercial usage.

- Group 17) Soda Ash—1:3.3 Silicate—TSPP
 18) Soda Ash—1:3.3 Silicate—TSP
 19) Soda Ash—Metasilicate—TSPP
 20) Soda Ash—Metasilicate—TSP
 21) TSPP - TSP—1:3.3 Silicate.

A comparison of Groups 17 and 18 indicated no essential differences other than that in hard water the combination containing TSPP was an improvement at 0.37% concentration, while that containing TSP was superior at 0.32%.

The substitution of metasilicate for 3.3 silicate (Groups 19 and 20) results in a general improvement