

AN INVESTIGATION OF THE
CHARACTERISTICS OF DENNISITE AND ITS COMPONENTS

Thesis by
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Acknowledgment

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Summary

1. The purpose of the research was to find a cheap method of breaking the double salt, Dennisite, into its components.
2. The properties of Dennisite are briefly described.
3. The following three possible ways of splitting Dennisite and recovering its components were tried.
 - a. Crystallization of tri-sodium phosphate from a super-saturated solution of Dennisite.
 - b. Separation of the phosphate as the comparatively insoluble tri-potassium octa hydrate.
 - c. Acidification of the Dennisite solution and crystallization of sodium tetra borate and sodium phosphate.
4. The acidification of the Dennisite solution was found to be the most satisfactory means of separating sodium tetra borate from the solution of the double salt.
5. The phase diagram shows clearly why acidification is effective in preventing the formation of Dennisite crystals, and indicates that all of the solid phases behave about the same at 45 as at 25 degrees, except that their solubilities are much greater.

History of the problem

In one stage of the process for the separation of borax from Searles Lake brine, as developed by "The American Potash and Chemical Company," a mixture of the crystals of borax ($\text{NaHBO}_3 \cdot 5\text{H}_2\text{O}$) and Dennisite ($\text{Na}_2\text{B}_2\text{O}_7 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$) is obtained. Searles Lake brine, being saturated with borax but not with Dennisite is used to wash this mixture of crystals. The borax remains unchanged, but the Dennisite goes into solution and is returned to the lake. Altho this results in a borax waste of only about three per cent, yet in a large capacity plant, the loss amounts to a very large number of tons per week. Provided the cost were sufficiently low, it would be desirable to split apart this double salt, change the meta borate to the tetra borate (borax) form, and sell the new product, tri-sodium phosphate, or change it to some other valuable form such as tri-potassium phosphate. For the plant at Trona, this last product would be a desirable one since one of the two chief products is now potassium chloride. This is sold largely to the fertilizer manufacturers for use in their commercial fertilizers. It would be very advantageous to substitute the phosphate for the chloride, because that would turn to profitable account a plant product that is now a complete loss, increase the value per unit of the potassium content, since the chloride makes it less desirable for use as a fertilizer, and at

the same time would reduce the freight charges, since it would make unnecessary the transportation of the part of the potash that has no value as a plant food.

Because the materials that might be produced ordinarily command a low price on the market, and because of the handicap of high freight rates imposed by the location of the source of raw materials, it is essential that any process that is developed, be one of low unit costs. The particular form in which the phosphate and the borate is obtained is not of great importance since, if sodium meta borate is obtained it could be put back into the plant cycle at a place where meta borate and tetra borate are kept in equilibrium by the presence of carbonate and bicarbonate. Phosphate can be sold in any form, but for the reasons pointed out above, in this particular case tri-potassium phosphate would be the most desirable.

Apparatus

It was thought to be best to attempt to solve this problem as one concerning the solubilities of the various salts that were apt to be encountered. To study these solubilities a bottle shaker was put in a water bath of about fifteen gallons capacity, that was heated by a five hundred watt immersion type electric heater, which was controlled by a mercury and glass regulator. This regulator contained about 150 cc of mercury, and the contact was made in a capillary tube of about 0.5 mm internal diameter. The contact was made with mercury on one side, and a copper plated platinum wire on the other. The whole contact tube was filled with distilled water to protect the copper amalgam. This type of a contact was found to be necessary to protect the relay contacts. At the same time, the regulator was very sensitive to temperature changes, and held the temperature of the thermostat very nearly constant. Such temperature changes as did take place could not be seen on a thermometer calibrated with 0.1 degree centigrade divisions.

The bottle shaker was made to fit the ordinary 100 cc oil sample bottles. Rubber stoppers, tightly wired into place were the only thing tried that was found to be satisfactory. Corks and sealing wax quickly dissolve in a saturated solution of tri-sodium phosphate at 45 degrees centigrade. Rubber stoppers however, are un-

affected at this temperature and are quite tight. The shaker was of the type that turns the bottles completely over about thirty times a minute.

Analytical methods

The following methods were used in the analysis of the aqueous solutions taken from the oil sample bottles.

Small tubes of filter paper, made to fit the end of a pipette were used to filter the solutions. Due to the high viscosity of some of the solutions however, this method was never very satisfactory. The filtering operation usually took so long that the liquid in the lower tube of the pipette would cool to such an extent that the solution would become greatly supersaturated and begin to form crystals. This would make it necessary to try another filter and pipette. A much more satisfactory method of sampling, especially at the higher temperatures was found to be the following procedure. Allow the bottles to remain suspended in the thermostat, after reaching equilibrium, for at least two full days, and preferably three or four. During this time the solid phases will settle to the bottom, leaving the supernatant liquid quite bright. Samples are removed from this liquid with a pipette and placed in a weighing bottle. That these solutions are quite free of any of the solid phases is indicated by two things, first, they are quite bright and second, by working rapidly it was usually possible to have the solutions in covered weighing bottles, cool to room temperature without crystals forming. Such

supersaturated solutions were very easily broken however, and when crystal formation had once started, it would be only a matter of seconds until the whole mass had become solid.

The most satisfactory method of obtaining samples for analysis was to remove from one to two grams of solution from the oil sample bottle as just described. This was weighed in a weighing bottle and the weight of the solution determined. It was then made into 100 cc of solution in a volumetric flask. Samples, varying from 5 cc to 25 cc, depending on the analysis to be made, and the concentration of the substance in the solution, were pipetted into conical flasks. Gravimetric work was done once, but the volumetric determinations were done either in duplicate or triplicate, depending on the accuracy desired, and the characteristics of the volumetric method to be used.

Analytical Procedure

Sodium salts of weak acids.

The solution from the volumetric flask was titrated with 0.1 normal HCl to the methyl orange end point. At this hydrogen ion concentration the borate is present as boric acid, the phosphate as the di-acid sodium salt, and the carbonate as CO_2 . The amount of acid used, thus gives a means of determining the amount of acid salt present in the sample.

Borate

Provided pure materials were used the sample can immediately be used for the borate titration. However, if any carbonate is present the sample must be acidified with 2 cc of 0.1 normal HCl beyond the end point, brought to boiling, cooled, and readjusted with 0.1 normal NaOH to the methyl orange end point. The solution can then be titrated with 0.1 normal NaOH to the phenolphthalein end point. When titrating borate with NaOH solution it is necessary to use some material that will form a stronger acid with boric acid. Two different things are commonly used; mannite is a convenient substance to use and is satisfactory for the purpose. Glycerine is just as satisfactory as far as the sharpness of the end point is concerned, and has the additional advantage of being more commonly available. In using glycerine it is

necessary to adjust it with sodium hydroxide solution to the phenolphthalein end point, since commercial glycerine is slightly acidic. Also, the glycerine must be examined occasionally, since it will slowly again become acidic on standing.

Whichever substance is used, it should be added until it will no longer decolorize the phenolphthalein. Two things are essential to the accuracy of this titration. The solution must be carbonate free, and the methyl orange must be used very sparingly or the end point of the borate titration will be obscured.

Phosphate

This determination was never fully satisfactory since it was seldom possible to check results to better than 2%. More commonly different determinations would vary as much as 5%. For the work being done, this was satisfactory, but changes in technique are clearly indicated. The method is not one with which great accuracy is possible, but with the proper technique, accuracy of 1% should be expected.

The method used was the yellow precipitate method for phosphate determination. The sample to be analyzed was made about five normal with nitric acid, and the phosphate precipitated with a large excess of ammonium molybdate solution. After having settled for a day, the yellow precipitate was filtered out, using a Watman's

R^o.

No. 44 filter paper, and washed with 5% KNO_3 solution until the wash water was neutral to litmus. The yellow precipitate was titrated with 0.1normal NaOH to the phenolphthalein end point.

Whenever phosphate is present in the solution a correction of the borate titration must be made, since in going from the methyl orange end point to the phenolphthalein end point, sodium hydroxide is used by the phosphate which changes from approximately the mono-sodium salt to the di-sodium salt. Correction is customarily made for this by allowing 95% of the sodium hydroxide that would be required for the quantitative conversion of all the phosphate present from the mono to the di-sodium salt, and subtracting this quantity from the amount found in the borate determination. The difference is the amount of sodium hydroxide actually required by the titration of the borate present.

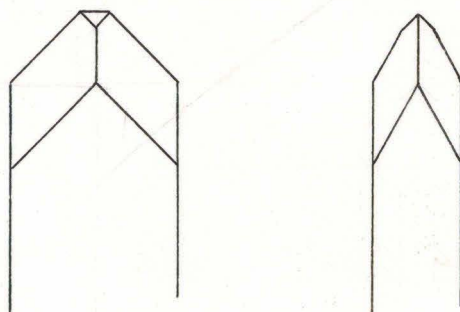
Determination of small amounts of borate.

In several of the solutions that contain large amounts of phosphate, there is only a small amount of borate in solution at equilibrium. Since, as was pointed out under the procedure for the determination of phosphate the determination of borate in the presence of a large amount of phosphate necessitates the determination of the difference between two large numbers, it is evident that

the method of borate determination outlined is not applicable to cases where only a very small amount of borate is found in the presence of a large amount of phosphate. Such samples were analyzed for borate by the method given by Noyes in his Qualitative Analysis. This method employs a set of color standards made up from alcohol, Hydrochloric acid, turmeric solution, and a known amount of the borate standard solution. A definite amount of the solution being analyzed is made up in the same way and its color compared with the standards. This method is quite sufficiently accurate for the cases mentioned, and determinations are made with fair accuracy that are quite impossible with the volumetric method given previously.

Dennisite

Dennisite is the hydrated double salt of sodium metaborate and tri-sodium phosphate ($\text{Na}_2\text{B}_2\text{O}_7 \cdot 2\text{Na}_3\text{PO}_4 \cdot 36\text{H}_2\text{O}$). The material crystallizes well, altho the first preparation in a laboratory may be difficult. The crystals may be quite large and well formed. They belong to the tetragonal system and have a characteristic appearance.



These crystals are of a pale yellow color when free of flaws. Another identifying characteristic is their melting point. They melt in their own water of crystallization sharply at 70.9degrees C. giving a clear liquid.

It was desired to determine roughly what the solubility curve of Dennisite was, and the following points were obtained. Those for 20 and 30 degrees are from Teeple.

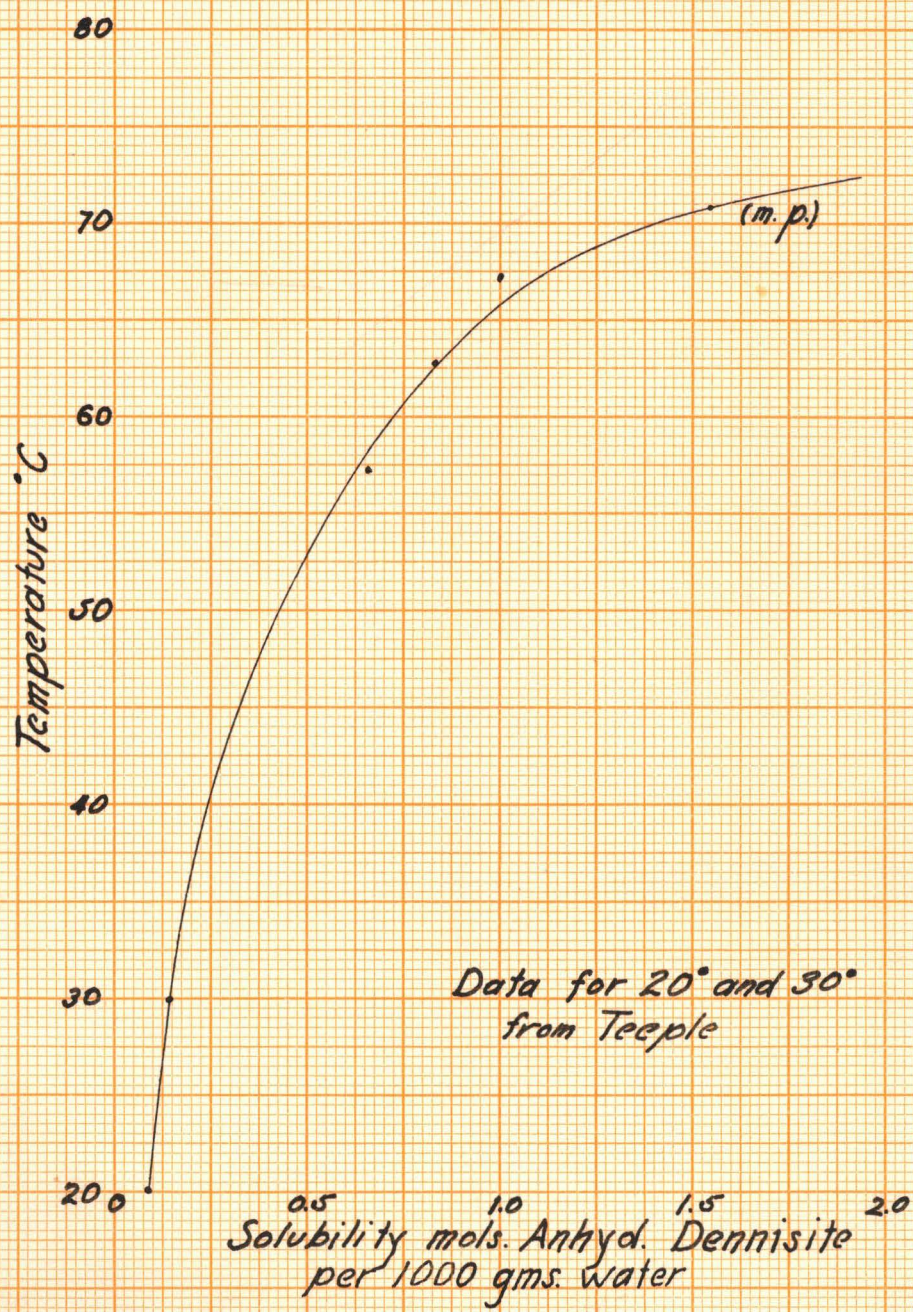
Temperature C	Anhyd. Dennisite mols/1000 gm. water
20.0	0.090
30.0	0.142
37.5	0.562
62.0	0.833

57.3	0.652
62.8	0.826
67.3	1.00
70.9	1.54 (m.p.)

These points are charted on an accompanying page.

Dennisite cannot be kept in the open air without decomposition. There is no rapid change, but after a few weeks, the crystals will accumulate a coating of sodium carbonate. This carbonate is stable in solution at the lower temperatures, but if the solution of carbonate covered Dennisite be heated above sixty or seventy degrees, CO_2 will be given off. Decomposition of the carbonate also occurs on acidification with a strong acid.

Dennisite Solubility Curve



Methods for splitting the double salt that were tried.

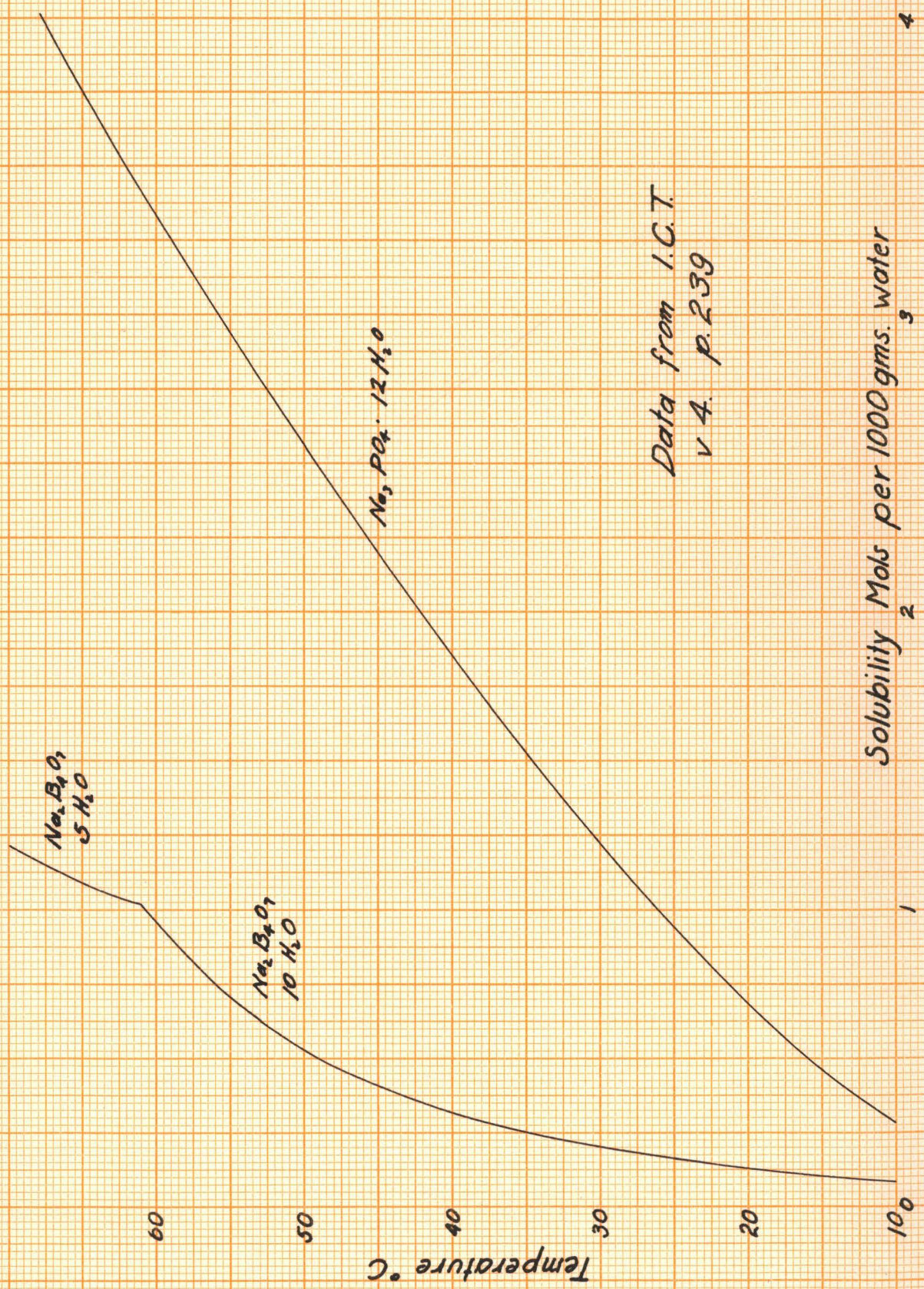
The first attempts to prepare Dennisite were unsuccessful because the solutions of borax, sodium hydroxide and tri-sodium phosphate, on cooling were able to supersaturate with respect to Dennisite to such an extent that tri-sodium phosphate would crystallize out. This suggested a simple and cheap method for recovering both the phosphate and the borate. However, once the double salt had been prepared, this method of separation would never work.

Another method was suggested by the report in Z. fur Phy. Ch. v127 p. 76 by Ernst Jänecke of a comparatively insoluble octa hydrate of tri-potassium phosphate that is stable below 45 degrees centigrade. Full directions for the preparation are given, but it was never possible to get the solid phase described in spite of numerous trials. Hence, this work had to be given up.

Another possible method of splitting the double salt, is to acidify the strong Dennisite solution and crystallize out borax and some phosphate salt, probably the di-sodium salt. A preliminary trial of this method was made, and by crystallizing from a solution that contained only 80% of the water that corresponds to the $36H_2O$ of the Dennisite present, and one half enough HCl to change the borate present to borax, and by seeding with commercial refined borax, a precipitate of sodium tetra borate was

obtained readily at 80 degrees centigrade. This indicated that work could profitably be done on the phase diagram of sodium meta borate, and tetra borate, and di-sodium and tri-sodium phosphate at the higher temperatures. The temperature of 45 degrees was chosen for two reasons. First, all of the solid phases at that temperature would be of a definite type. All of the hydrated salts would be at least 5 degrees removed from any transition temperature. And second, work at 45 degrees should be similar in technique to the work that is commonly done at the lower temperatures. Investigation of this phase diagram at 45 degrees thus should serve as a means of developing a technique that should be applicable to 60 degrees or higher, and at the same time should supply information regarding the changing behavior of these salts with increasing temperature.

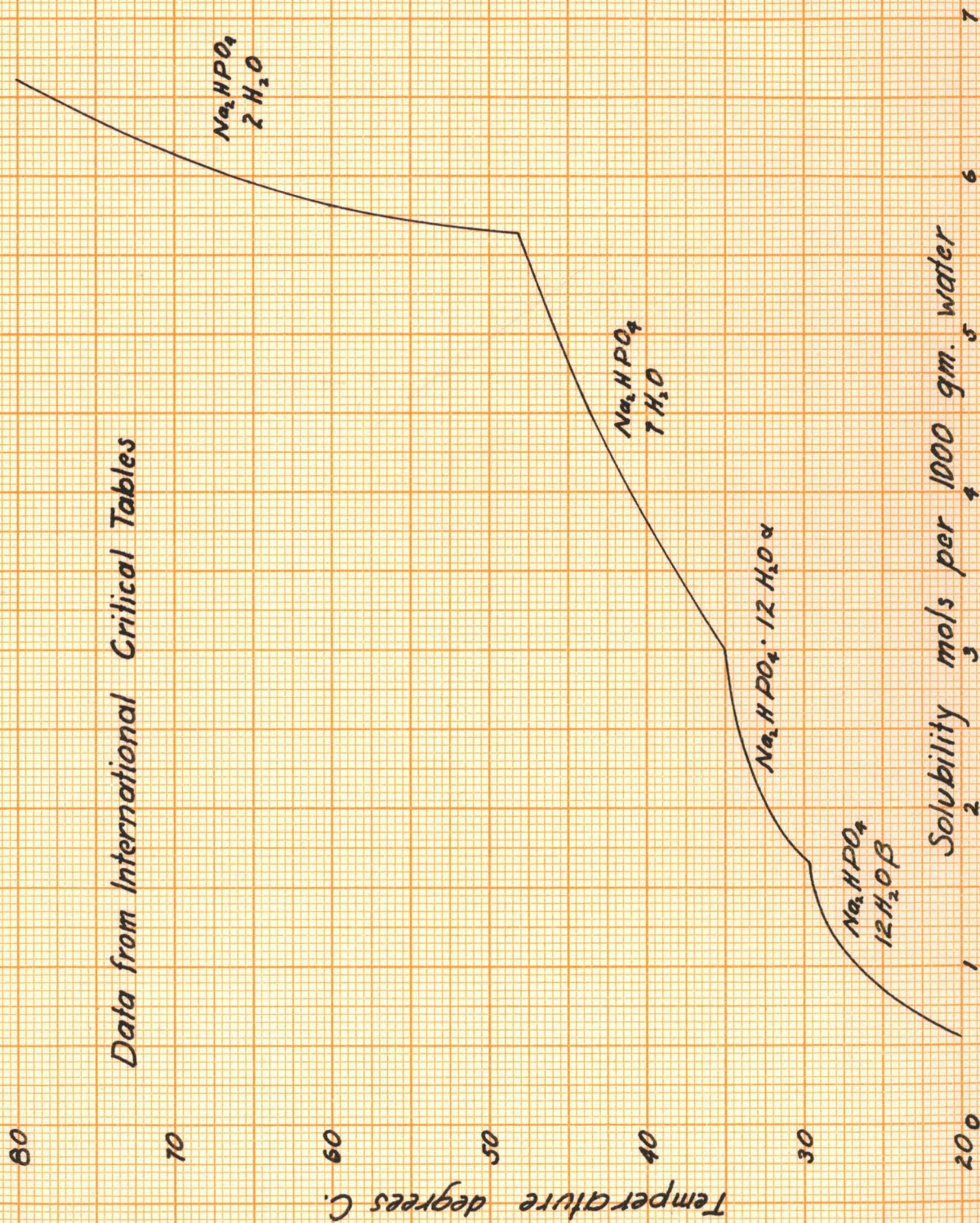
When working up this phase diagram, full advantage was taken of all the solubility data given in the literature for the substances concerned. The complete diagram, worked out in considerable detail is given in the book by Teeple "Development of Searles Lake Brine". This phase diagram is only given however, for the one temperature of 25 degrees centigrade. Data is to be found in the reference tables for the solubility - temperature curves of tri-sodium, and di-sodium phosphate, also for sodium tetra borate. These curves are included in this report.



Data from I.C.T.
v 4. p.239

Solubility Mols per 1000 gms. water

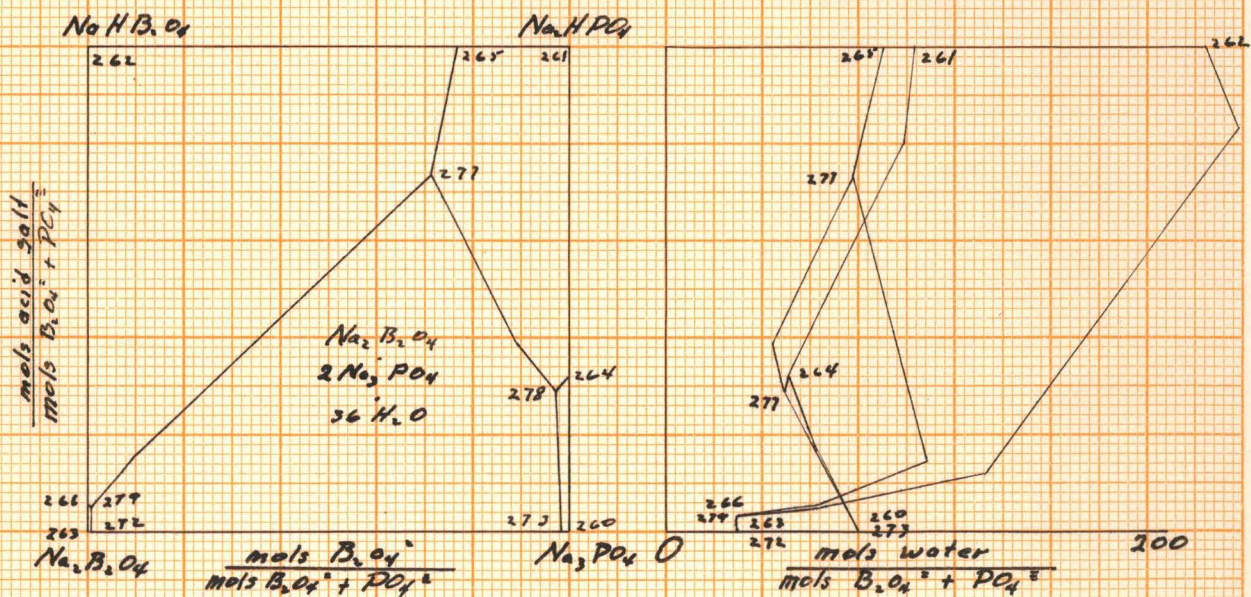
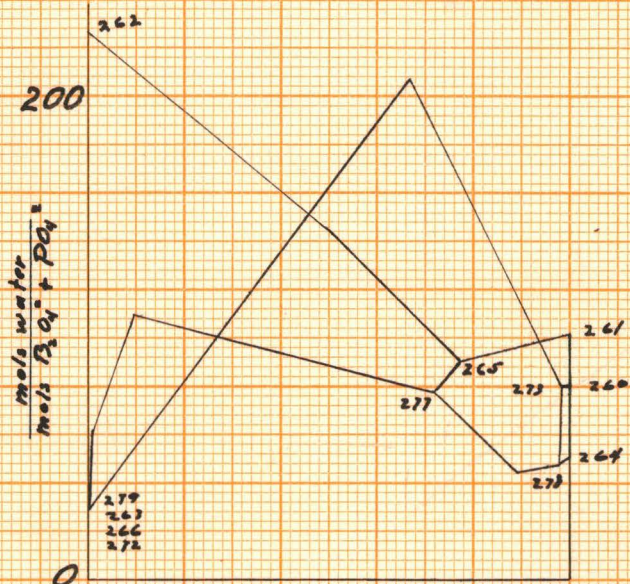
Data from International Critical Tables



Data from Teeple for phase diagram at 25 Degrees C.
 Ref. The Industrial Development of Searles Lake Brines
 Chemical Society Monograph No.49 Published by the
 Chemical Catalogue Co.
 Chemical Catalogue Co.

Point	mols water		mols B_2O_3		mols acid salt	
	mols B_2O_3	PO_4	mols B_2O_3	PO_4	mols B_2O_3	PO_4
260	79.6		0		0	
261	102.5		0		1	
262	224		1		1	
263	28.5		1		0	
264	50.5		0		.318	
	66.3		0		.132	
	98		0		.803	
265	90		.234		1	
	145		.522		1	
	238		1		.833	
	132		1		.118	
	61.7		1		.043	
266	28.3		1		.028	
272	28.7		.998		0	
	208		.333		0	
273	80		.016		0	
278	48.1		.024		.288	
	44.2		.115		.394	
277	77.5		.287		.729	
	109		.907		.147	
279	28.5		.999		.026	

Temperature 25°C



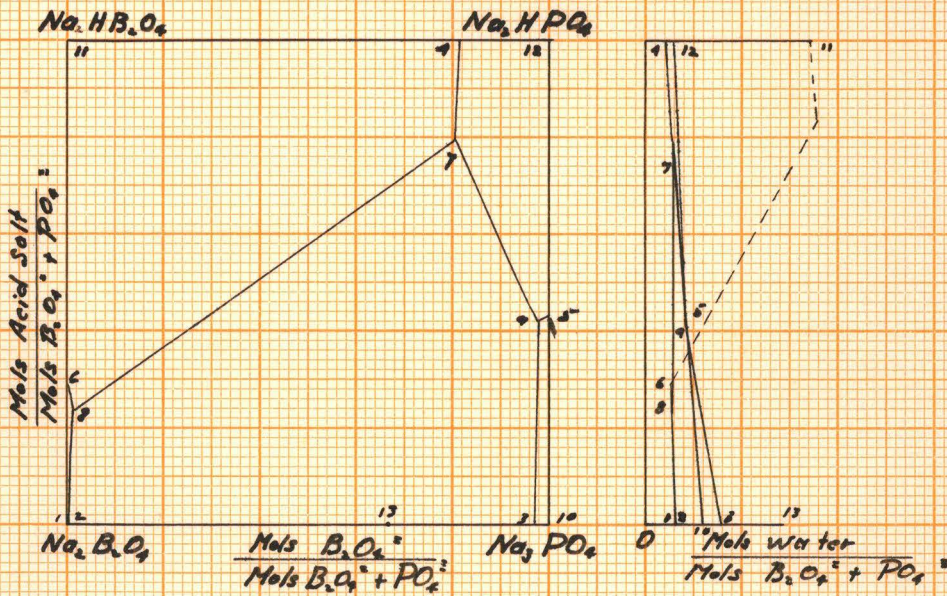
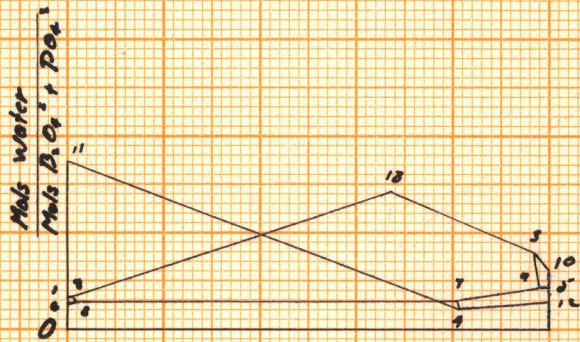
Data from Teeple
Development of Searles Lake Brine

Data for the phase diagram at 45 degrees C

Point	mols water		mols B_2O_3		mols acid salt	
	m B_2O_3	PO_4	mols B_2O_3	PO_4	mols B_2O_3	PO_4
1	12.8		1		0	
2	13.0		.994		0	
3	32.1		.0284		0	
4	8.23		.185		1	
5	17.1		0		.436	
6	10.4		1		.283	
7	11.8		.192		.797	
8	10.8		.988		.233	
9	17.1		.0202		.416	
10	25.2		0		0	
11	69.3		1		1	
12	11.5		0		1	
13	56.9		.333		0	

Temperature 45°C

200



200

Conclusions

The work done shows clearly that it is possible to crystallize tri-sodium phosphate from a supersaturated solution of Dennisite. This method is not apt to be useful because of the probability of precipitating Dennisite out of the supersaturated solution.

Also, by adjusting the hydrogen ion concentration of the solution it is possible to break Dennisite into its two components. The work done indicates that this process should take place, either at a low temperature, 25 degrees or less, or at a temperature somewhat above 45 degrees centigrade. This is because 45 degrees offers few advantages over 25 degrees and at the same time the solutions are much more difficult to handle. However, the extremely high solubility of Dennisite at a somewhat higher temperature indicates that the phase diagram at such a temperature would be more favorable to the object of this work.

As to the technique to be employed at higher temperatures the equipment used in this work should be quite satisfactory, except that the thermostat must be filled with oil rather than water, since even at 45 degrees evaporation was quite rapid. Rubber stoppered oil sample bottles should be quite satisfactory at 60 degrees, and possibly above. Settling of the solid phase rather than filtration of the sample must be used.

The small change in the appearance of the phase diagram with a twenty degree rise in temperature is quite noticeable, especially when one considers the great change in the solubility charts. It is evident that only small changes in the character of the constituents could have taken place with the rise in temperature. The system at 45 degrees is very much the same as at 25 degrees except that everything is more soluble at the higher temperature.