The Role of Catalysis in the Preparation and Reactions of Some Cobaltic and Chromic Ammines

By JOHN C. BAILAR, JR., AND J. B. WORK[1]

Several investigators have observed that metal ammines in water solution are partly or completely decomposed by contact with extended surface catalysts.

Schwarz and Kronig[2] found that hexammine cobaltic chloride, when shaken with decolorizing charcoal or silica gel, is converted to chloropentammine cobaltic chloride, $[Co(NH_3)_5Cl]Cl_2$. Shilov and Nekrasov[3] extended this study to a wide range of cobaltic ammines and double salts and found, in every case, that the complex ion was decomposed. Shukoff and Shipulina[4] showed the same effect with coördination compounds of platinum. On the other hand, G. W. Smith[5] observed that many complex ions are adsorbed on silica gel without decomposition.

It remained for Bjerrum[6] to utilize this catalytic effect in the preparation of cobaltic ammines. With the aid of activated carbon, he was able to prepare hexammine cobaltic chloride from cobaltous chloride, ammonium hydroxide, ammonium chloride and air at atmospheric temperature and pressure—a great advance over the cumbersome methods previously used.

This article reports some supplementary observations on such catalysis and its use in the study of coördination compounds. Preliminary experiments showed that decolorizing charcoal, silica gel and Raney nickel all catalyze reactions involving the coördination of nitrogen to cobalt. The reactions trans-$[Co\ en_2Cl_2]Cl + 2NH_4OH \rightarrow [Co\ en_2(NH_3)_2]Cl_3 + 2H_2O$,[7] and $[Co(NH_3)_5-Cl]Cl_2 + NH_4OH \rightarrow [Co(NH_3)_6]Cl_3 + H_2O$ were used to compare the three catalysts. In the absence of a catalyst, ammonium hydroxide converts $[Co\ en_2Cl_2]Cl$ to $[Co\ en_2(NH_3)Cl]Cl_2$ readily, but the replacement of the second chlorine proceeds slowly and incompletely, most of the final product being $[Co\ en_2(NH_3)Cl]Cl_2$. In the presence of silica gel, a sample of $[Co\ en_2Cl_2]Cl$ was completely converted to $[Co\ en_2(NH_3)_2]Cl_3$ in thirty minutes; in the presence of either charcoal or Raney nickel the same effect was produced in two minutes. The second reaction cited is so slow as to be almost imperceptible in the absence of a catalyst. In the presence of silica gel, it was not complete in twenty-four hours; under the

same conditions, but with charcoal present, it was complete in five hours. The catalytic properties of Raney nickel are comparable with those of charcoal; it is not as easy to use, however, for it is sometimes very difficult to filter.

The present study has shown that many reactions in which nitrogen is coördinated to cobalt or chromium are particularly susceptible to catalysis by charcoal. It seems to be immaterial whether the nitrogen is part of a nitro group, a primary amine, or ammonia.

Preparation of Triethylenediamine Chromic Chloride.—The usefulness of this catalytic effect is well illustrated by the preparation of triethylenediamine chromic chloride. In the past, this preparation has necessitated the use of anhydrous materials, for water molecules coördinated to chromium are not displaced by amines under ordinary conditions. However, in the presence of charcoal, hydrated chromic chloride and aqueous ethylenediamine react readily to give the luteo salt. Even with the aid of a catalyst, however, aqueous ammonia is not able to displace water molecules from the coördination sphere to form $[Cr(NH_3)_6]Cl_3$.

Mutual Replacement of Ammonia Molecules and Nitro Groups.—Particularly interesting is the ease with which ammonia molecules and nitro groups displace each other from the cobalt coördination sphere. Both of these groups are so firmly linked to the metal that under ordinary circumstances they are removed only with difficulty.

Werner's[8] discovery that either ammonia or chlorine, or both, can be expelled from the coördination sphere of $[Co\ en_2(NH_3)Cl]^{++}$ by the action of nitrites is an unusual exception. In the presence of charcoal, $[Co\ en_2(NH_3)Cl]^{++}$ and sodium nitrite react smoothly and quickly at room temperature to give $[Co\ en_2(NH_3)(NO_2)]^{++}$, and on warming, $[Co\ en_2(NO_2)_2]^{+}$. In the absence of charcoal, $[Co\ en_2(NH_3)_2]^{+++}$ does not seem to react with nitrites, but when charcoal is present, it is readily converted into $[Co\ en_2(NO_2)_2]^{+}$. Similarly, in the presence of charcoal, the very stable $[Co(NH_3)_6]^{+++}$ ion is converted to $[Co(NH_3)_3(NO_2)_3]$ by heating with aqueous sodium nitrite.

Without a catalyst, nitro groups are expelled from the coördination sphere by aqueous ammonia only in rare cases, and even by liquid ammonia, very slowly. Werner[9] observed a case of such replacement in the reaction of trans-$[Co\ en_2-$

(1) From a portion of the doctorate thesis of J. B. Work, 1942.

(2) Schwarz and Kronig, Ber., 56, 208–214 (1923).

(3) Shilov and Nekrasov, Z. physik. Chem., 118, 79–88 (1925); Nekrasov, J. Russ. Phys.-Chem. Soc., 58, 207–214 (1926).

(4) Shukoff and Shipulina, Kolloid-Z., 49, 126–133 (1929).

(5) G. W. Smith, J. Chem. Education, 18, 432 (1941).

(6) Bjerrum, "Metal Ammine Formation in Aqueous Solutions. Theory of Reversible Step Reactions," P. Haase and Son, Copenhagen, Denmark, 1941.

(7) The symbol "en" represents one molecule of ethylenediamine.

(8) Werner, Ann., 386, 168 (1912).

(9) Werner, ibid., 386, 55 (1912).

$(NO_2)_2]^+$ with a mixture of aqueous ammonia and ammonium chloride to give [Co en$_2$(NH$_3$)-(NO$_2$)]$^{++}$. In the presence of charcoal, however, liquid ammonia converts [Co(NO$_2$)$_6$]$^=$ and [Co-(NH$_3$)$_2$(NO$_2$)$_4$]$^-$ to [Co(NH$_3$)$_3$(NO$_2$)$_3$]. There is some evidence that the reaction may continue very slowly to the formation of [Co(NH$_3$)$_4$-(NO$_2$)$_2$]$^+$. We were never able to make this step of the reaction go to completion, however.

It is worthy of note that [Co(NH$_3$)$_3$(NO$_2$)$_3$] is the stable end-product in the displacement of ammonia from [Co(NH$_3$)$_6$]$^{+++}$ and in the displacement of nitro groups from [Co(NO$_2$)$_6$]$^=$. It seems to indicate that ammonia and nitro groups coordinate to cobalt with approximately the same bond strength. The low solubility of [Co-(NH$_3$)$_3$(NO$_2$)$_3$] may also be a factor.

Introduction of Monoamines into the Coördination Sphere.—Several attempts were made to induce organic amines to react with [Co en$_2$Cl$_2$]Cl to form compounds of the type [Co en$_2$(RNH$_2$)$_2$]-Cl$_3$, where R represents an alkyl or aryl group. Previous workers[10] have been able to introduce one amine group into the coördination sphere, and it was hoped that by the use of a catalyst the second step of the reaction might be effected. However, the presence of charcoal favors a very different reaction, which results in the formation of triethylenediamine cobaltic chloride. Methylamine, isopropylamine, aniline and pyridine, all of which yield [Co en$_2$(RNH$_2$)Cl]$^{++}$ readily in the absence of a catalyst, induce complete conversion to the triethylenediamine salt. Ablov[10] has found that organic amines weaker than aniline produce this effect, even in the absence of charcoal. On the other hand, treatment of an aqueous solution of the dichlorodiethylenediamine salt with charcoal alone produces none of the triethylenediamine salt, either in a neutral solution or one made strongly basic with sodium hydroxide. Apparently the organic amine coördinates with the cobalt, but rearrangement then displaces it by the more strongly coördinating ethylenediamine. Similar cases have been observed in reactions of optically active diamines with cobalt complexes containing enantiomorphic diamine molecules.[11] Thus [Co(l-propylenediamine)$_2$Cl$_2$]Cl reacts easily with dextro-propylenediamine, but the product formed, [Co(l-pn)$_2$(d-pn)]Cl$_3$, is so unstable that it immediately rearranges to a mixture of [Co-(l-pn)$_3$]Cl$_3$ and [Co(d-pn)$_3$]Cl$_3$, both of which are stable. In the present instance, only one product of the rearrangement, [Co en$_3$]Cl$_3$, is stable enough to be isolated, since the monoamines used do not have strong donor properties.

Search for a Walden Inversion.—If one optically active material is converted into another, the product may have the same configuration as the parent compound, or the enantiomorphic configuration. Obviously, two different reaction mechanisms are involved, and it is possible that the presence of a catalyst might favor one or the other of these to give a preponderance of the product which is obtained in lesser amount in the absence of a catalyst—a Walden inversion would thus be observed. The reaction between levo-[Co en$_2$Cl$_2$]$^+$ and nitrites in the presence of cobaltous ion and in the absence of any catalyst has been investigated in this laboratory.[12] The product under all conditions tried was dextro-[Co en$_2$(NO$_2$)$_2$]$^+$. The use of charcoal as a catalyst gives the same product. Dextro-[Co en$_2$-(NH$_3$)Cl]$^{++}$ gives dextro-[Co en$_2$(NH$_3$)(NO$_2$)]$^{++}$. The reaction of levo-[Co en$_2$Cl$_2$]$^+$ with aqueous ammonia, in the absence of a catalyst, displaces one chloro group from the complex to give dextro-[Co en$_2$(NH$_3$)Cl]$^{++}$, but is unable to displace the other. Both the levo-dichloro and the dextro-chloro-ammino-ions react with aqueous ammonia in the presence of charcoal to yield an [Co en$_2$-(NH$_3$)$_2$]$^{+++}$ which shows no optical activity. This is mostly the trans salt, and may be all trans. This rearrangement to the trans form is interesting in view of the fact that aqueous ammonia (in the absence of charcoal) produces only the cis form of [Co en$_2$(NH$_3$)Cl]Cl$_2$ from either cis- or trans-[Co en$_2$Cl$_2$]Cl.

Experimental

Preparation of Triethylenediamine Chromic Chloride.—To 13.3 g. of green chromic chloride hexahydrate (0.05 mole) mixed with 1.5 g. of decolorizing charcoal, 19 g. of 57% ethylenediamine (0.18 mole) was added. The mixture was heated as hot as possible in an open beaker on a steam cone overnight, and after cooling was covered with 50 cc. of alcohol. After an hour the mixture was ground in a mortar, the alcohol was filtered off, and the process was repeated with smaller portions of alcohol until all of the excess ethylenediamine had been removed. After drying, the residue was stirred with 25 cc. of 1.7 N hydrochloric acid at 60° for a minute, and the mixture was quickly filtered into a well cooled mixture of 40 cc. of alcohol and 25 cc. of concentrated hydrochloric acid. The orange [Cr en$_3$]Cl$_3$·3.5H$_2$O was removed by filtration, washed with alcohol and ether, and dried in air; yield, 8.3 g., or 40% of the theoretical.

Replacement of Ammonia by Nitro Groups.—Three grams of mixed cis- and trans-[Co en$_2$(NH$_3$)$_2$]Cl$_3$ (0.0094 mole) was mixed with 10 g. of sodium nitrite (0.145 mole), 1 g. of charcoal, and 30 cc. of water. The mixture was warmed on a steam-bath until no more ammonia was evolved (about two hours), cooled to room temperature and filtered. The residue was washed with 10 cc. of hot water. When the filtrate and washings were cooled, 0.6 g. of a mixture of yellow and brown crystals was obtained. That the material was a salt of the ion [Co en$_2$(NO$_2$)$_2$]$^+$ was shown by the fact that warming it with hydrochloric acid liberated nitrogen dioxide fumes and formed a red solution that quickly turned green, depositing almost the theoretical quantity of trans-[Co en$_2$Cl$_2$]Cl when cooled. The dinitro salt must have been mostly of the cis configuration.

Two and seven-tenths grams of [Co(NH$_3$)$_6$]Cl$_3$ (0.01 mole) and 10 g. of sodium nitrite (0.145 mole) were dissolved in 30 cc. of water and heated on the steam cone for thirty minutes. No ammonia could be detected above

(10) Several studies have been made. Recent ones are those of Ablov, Bull. soc. chim., [5] 3, 2278 (1936); 4, 1792 (1937), and of Bailar and Clapp, THIS JOURNAL, 67, 171 (1945).

(11) Bailar, Stiegman, Balthis and Huffman, THIS JOURNAL, 61, 2402 (1939).

(12) McReynolds and Bailar, ibid., 60, 2817 (1938). Other work to be published later.

the solution by odor or litmus test. But when the experiment was repeated with the addition of one gram of charcoal, ammonia was evolved as soon as the mixture was warmed. A slow stream of air was passed through the mixture to keep the carbon suspended and to aid in the escape of ammonia. After three hours the mixture was filtered. Fully two liters of water were required to wash all of the yellow salt out of the charcoal, which was then found to contain no cobaltous or cobaltic hydroxides. When the initial filtrate was cooled about a gram of fine yellow crystals precipitated. This material was $[Co(NH_3)_3$-$(NO_2)_3]$, as was shown by analysis and by the very low conductivity of a solution made from it. Qualitative tests of the solution from which these crystals had precipitated showed the absence of $[Co(NO_2)_6]^{=}$, $[Co(NH_3)_4(NO_2)_2]^{+}$ and $[Co(NH_3)_2(NO_2)_4]^{-}$ ions. Anal. of the crystals, calcd. for $[Co(NH_3)_3(NO_2)_3]$: N, 33.87. Found: N, 33.36, 33.31.

Small samples (0.2 g.) of several nitro cobaltic coördination compounds were treated with an excess of liquid ammonia, both in the presence and in the absence of charcoal. Qualitative tests on the residues showed that $[Co(NH_3)_5$-$NO_2]Cl_2$ and $[Co en_2(NO_2)_2]Cl$ were not affected in either case. Trinitrotriammine cobalt was scarcely attacked by ammonia alone, but was partially converted to $[Co(NH_3)_4$-$(NO_2)_2]NO_2$ in the presence of charcoal. Erdmann's salt, $NH_4[Co(NH_3)_2(NO_2)_4]$, which was very slightly attacked in the absence of the catalyst, was completely converted to $[Co(NH_3)_3(NO_2)_3]$ when charcoal was present. Sodium cobaltinitrite was partially converted to the same product in the absence of catalyst, but completely in its presence.[13]

Reaction of $[Co en_2Cl_2]Cl$ with Organic Amines in the Presence of Charcoal

Pyridine.—One-half gram of charcoal, 2.8 g. of trans-$[Co en_2Cl_2]Cl$ (0.01 mole), 2.1 g. of pyridine (0.0267 mole), and 25 ml. of water were shaken in a closed flask for four days without appearance of the yellow color which would be indicative of the formation of a luteo type salt. The mixture was therefore heated to about 80° for eight hours, cooled, and filtered. The filtrate was mixed with 75 ml. of alcohol; this mixture was stirred for a few minutes and filtered. The filtrate contained cobaltous salts. The yellow residue was washed with alcohol and with ether and dried in air. The yield was 1.7 g. of impure salt. The material was recrystallized and dried at 110° for five hours. Anal. Calcd. for $[Co en_2py_2]Cl_3$: Cl, 24.02. Calcd. for $[Co en_3]Cl_3$: Cl, 30.78. Found: Cl, 30.60.

In the hope that $[Co en_2py_2]^{+++}$ might be obtained under less strenuous conditions, 1 g. of $[Co en_2pyCl]Cl_2$ (0.0027 mole), 2 cc. of pyridine (0.25 mole), and 0.5 g. of charcoal were ground together in 5 cc. of water at room temperature for several hours. No reaction took place.

Aniline.—Fifteen grams of trans-$[Co en_2Cl_2]Cl$ (0.0525 mole), 1 g. of charcoal, 15 g. of aniline (0.161 mole), and 20 ml. of water were heated to 90° for one and a half hours. The charcoal was removed by filtration and alcohol was added to the black filtrate. A brownish compound precipitated; it was shown to be $[Co en_3]Cl_3$ contaminated by decomposition products of the aniline. Several recrystallizations gave a pure yellow compound which was dried at 110° for six hours. Anal. Calcd. for $[Co en_3an_3]Cl_3$: Cl, 22.56. Calcd. for $[Co en_3]Cl_3$: Cl, 30.78. Found: Cl, 30.74.

Isopropylamine.—Six grams of trans-$[Co en_2Cl_2]Cl$ (0.021 mole), 9.6 g. of isopropylamine (0.162 mole), and 1 g. of charcoal were ground in a mortar for thirty minutes. About 50 ml. of 95% alcohol was added and the mixture was stirred for several minutes and filtered. The residue was washed with alcohol until all isopropylamine had been removed and was then dissolved in 25 ml. of

water, forming a solution to which was added 150 ml. of alcohol and then 100 ml. of ether. This mixture was filtered after four hours. The yellow residue was recrystallized and dried at 110° for five hours. Anal. Calcd. for $[Co en_2ip_2]Cl_3$: Cl, 26.35. Calcd. for $[Co en_3]Cl_3$: Cl, 30.78. Found: Cl, 30.87.

Reactions of Optically Active Ions.—About 0.5 g. of decolorizing charcoal was mixed intimately with 0.1054 g. of levo-$[Co en_2Cl_2]Cl$. To this mixture was added a solution of one gram of sodium nitrite in 20 ml. of water. The mixture was stirred for five minutes and filtered. The residue was washed until all $[Co en_2(NO_2)_2]NO_2$ was removed; the washings were combined with the filtrate and the resulting solution was diluted to exactly 100 ml. This solution was then 0.117% $[Co en_2(NO_2)_2]NO_2$; the optical rotation was found to be +0.045°, $[\alpha]_D$ +38.5. Since a 1.0% solution[14] of dextro-$[Co en_2(NO_2)_2]NO_2$ has $[\alpha]_D$ +41.5°, it is obvious that more than 90% of the $[Co en_2(NO_2)_2]NO_2$ was dextro-cis; little racemization or formation of trans salt had taken place.

One-half gram of charcoal, 0.241 g. of dextro $[Co en_2$-$(NH_3)Cl]Cl_2$ (0.0008 mole), 3.0 g. of sodium nitrite (0.044 mole), and 15 ml. of water were mixed and stirred occasionally for two hours. The charcoal was removed by filtration and washed with water until the washings were colorless. The deep orange filtrate was combined with the washings and diluted to exactly 50 ml., giving a 0.5% solution if calculated as $[Co en_2(NH_3)(NO_2)]Cl_2$. For this solution, $[\alpha]_C$ +8.8° and $[\alpha]_D$ +16.8°; $[\alpha]_E$ could not be determined accurately due to the depth of color of the solution. The accepted values[15] for a 0.1% solution of dextro-$[Co en_2(NH_3)(NO_2)]Br_2$ are $[\alpha]_C$ +20° and $[\alpha]_D$ +50°.

To one gram of levo-$[Co en_2Cl_2]Cl$ in 2.5 ml. of 20% ammonium hydroxide, 0.5 g. of decolorizing charcoal was added. The mixture was stirred for twenty minutes and the charcoal was removed by filtration and washed with a few milliliters of water. The addition of 50 ml. of 95% alcohol to the combined filtrate and washings precipitated an oil. This was separated from the supernatant liquid by decantation, and was then stirred with 20 ml. of absolute alcohol. This treatment gave a semi-crystalline mass which, after removal of the alcohol by decantation, was dissolved in 2 or 3 ml. of water and reprecipitated by the addition of 50 ml. of alcohol containing about 10% hydrochloric acid. The yellow crystalline precipitate was washed with alcohol and with ether and dried in air. The yield of $[Co en_2(NH_3)_2]Cl_3$ was 0.4 g. An 0.5% solution of the product showed no optical rotation at the C, D or E lines. A concentrated solution of the product was mixed with sodium dithionate and allowed to stand. After a day, a considerable amount of the insoluble orange trans-dithionate had precipitated.

Two grams of dextro-$[Co en_2(NH_3)Cl]Cl_2$, one gram of carbon black, and 10 ml. of concentrated ammonium hydroxide were stirred together for ten minutes. The charcoal was then removed by filtration and washed with small portions of water. The filtrate and washings were combined and mixed with 120 ml. of absolute alcohol. An oil precipitated; it was converted to pure crystalline $[Co en_2$-$(NH_3)_2]Cl_3$ by a method similar to that described above. The yield was 1.6 g. An 0.5% solution of the product showed no optical activity at the C, D or E lines. The addition of sodium dithionate to a saturated solution of it precipitated some orange trans-dithionate.

In both cases, the solution may still have contained cis salt, for it remained orange. It is clear, however, that formation of the trans salt rather than racemization was largely responsible for the inactivity of the product.

Summary

It has been shown that extended surface catalysts, such as charcoal, silica and Raney nickel, catalyze the formation of Co–N and Cr–N coördi-

(13) Several other complex salts were shown to be unattacked by liquid ammonia in the presence as well as in the absence of charcoal. These include $K_3[Co(CN)_6]$, $[Co(NH_3)_4CO_3]NO_3$, $K_3[Cr(CN)_6]$, $[Cr py_2 Cl_2]$, $NH_4[Cr(NH_3)_2(NCS)_4]$, and $[Cr(NH_2CH_2COO)_3]$. All of these have extremely stable coördination bonds.

(14) Werner, Ber., **44**, 2447 (1911).

(15) Wilbuschewitsch, Dissertation, Zürich, 1919.

nate bonds. Charcoal seems to be the most suitable catalyst for practical purposes.

In the presence of charcoal, aqueous ammonia displaces both chlorides from cis-[Co en$_2$Cl$_2$]$^+$, giving preponderantly the *trans* product, [Co en$_2$(NH$_3$)$_2$]$^{+++}$. In the absence of the catalyst, only one ammonia molecule enters the coördination sphere, and the product [Co en$_2$(NH$_3$)Cl]$^{++}$ has the *cis* configuration, irrespective of whether the dichloro salt was *cis* or *trans*.

Triethylenediamine chromic chloride is readily prepared by the reaction of hydrated chromic chloride and hydrated ethylenediamine in the presence of charcoal.

In the presence of charcoal, sodium nitrite reacts with hexammine cobaltic ion and ammonium hydroxide reacts with cobaltinitrite to give trinitrotriammine cobalt, which thus seems to be the most stable member of the cobalt nitro ammine series.

Organic amines react with the dichlorodiethylenediamine cobaltic ion to give ions of the type [Co en$_2$(RNH$_2$)Cl]$^{++}$ if no catalyst is present, but in the presence of charcoal, complete rearrangement to the extremely stable [Co en$_3$]$^{+++}$ ion takes place.

The presence of charcoal during reactions of optically active cobalt ammines does not alter the sign of rotation of the products.

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The System Aluminum Sulfate–Ethanol–Water at 30° and 80°

By Edwin A. Gee[2]

Introduction

This investigation was undertaken to establish the 30 and 80° isotherms of the system aluminum sulfate–ethanol–water and to determine the various hydrates present at equilibrium.

A method for the preparation of iron-free aluminum sulfate using ethyl alcohol as a solvent was brought to the attention of the Bureau of Mines by Dr. P. S. Roller of the Bureau staff. In the pilot-plant development that followed, data on the system aluminum sulfate–ethanol–water were necessary to interpret certain phenomena that had been observed. Systems of the general type (inorganic salt–ethanol–water) have been previously investigated.

Experimental Methods

Solvent.—Ethanol–water mixtures were prepared from distilled water and purified ethyl alcohol. Commercial 95% alcohol was refluxed for several hours over lime and distilled; the distillate was redistilled to ensure complete separation from the lime. Density determinations were made to establish solution composition, pycnometers of 50-ml. capacity being used.

Aluminum Sulfate.—Baker analyzed aluminum sulfate was employed throughout.

Solubility Determinations.—Saturation was effected in 250-milliliter bottles which were rotated four to six days in two water-baths operated at 30 ± 0.01° and 80 ± 0.2°, respectively. When equilibrium was approached from undersaturation aluminum sulfate was added directly to the solvent. Approach from supersaturation was simulated by adding concentrated aqueous aluminum sulfate solution to the alcohol. After equilibrium was reached the mixtures were allowed to settle and were filtered through sintered glass of fine size.

Alcohol content was determined by distillation to dryness, the composition of the distillate being determined by density. This method yielded alcohol percentages accurate within 1 to 2% and this limited the over-all accuracy of the

investigation. Aluminum sulfate solubility was determined by direct evaporation and ignition of the liquid sample or by precipitation with ammonia. Water was calculated by difference. The density of the equilibrium solutions was measured in 50-milliliter pycnometers.

Points near the plait point were determined by titrating two-phase liquid systems with water to homogeneous solutions.

Identification of Solid Phases.—Analysis of the solid phase was made by two methods. In the first, the crystals were separated from the mother liquor by filtration after which they were successively washed with absolute alcohol and anhydrous ether. The water of hydration was then determined by ignition. This method had a tendency to give low results in determination of the higher hydrates. This was probably due to the dehydration effect of the anhydrous alcohol and ether which were necessary to obtain a rapidly drying product. The second method is essentially an application of the work of Foote and Sholes in which the hydrates of inorganic salts in equilibrium with various alcohol mixtures are determined.[3] If a slightly soluble salt of known hydrate is placed in an alcohol–water mixture the specific gravity of the alcoholic solution will increase or decrease according to the release or absorption of water by the salt. If no change is noted the hydrate is in equilibrium with that alcoholic solution. Thus, by observing the change in specific gravity of the solvent the solid phase present at equilibrium with various alcoholic mixtures can be identified. This method necessitated the preparation of known hydrates which were prepared by precipitation of aluminum sulfate from alcohol–water mixtures. The various hydrates were dried over correspondingly lower hydrates. The final hydrate composition was determined by ignition.

The technique required slight modification for application to this investigation. As several hydrates are present at the same temperature, there must be a transition point at which two hydrates will be in equilibrium with the same alcoholic solution. After the approximate location of this transition point had been ascertained, its position could be established by adding a mixture of the two hydrates involved and observing the change in composition.

Results and Discussion

The results of the investigation at 30 and 80° are recorded in Table I and Fig. 1 and in Table II

(3) H. W. Foote and S. R. Sholes, THIS JOURNAL, 33, 1309 (1911).