appears much too low, indicating that fusion may not have been complete.

The heat content curve for pyrite is regular. At the highest temperature point in Table I, the dissociation pressure is estimated as 1.8 atm. The alloy capsule failed just beyond this point because of increased pressure.

Table II lists smooth values of the heat contents above 298.16°K. at even temperatures and at transition and melting points. The corresponding entropy increments also are listed, having been calculated by the method of Kelley.[11]

The heat content data for the three substances are represented by the relationships below, the temperature range of validity and the average degree of fit being shown in parentheses.

Subst.	$H_T - H_{298.16} =$	
MnS(c)	$11.40T + 0.90 \times 10^{-3}T^2 - 3479$	(298–1803°K., 0.5%)
FeS(α)	$5.19T + 13.20 \times 10^{-3}T^2 - 2721$	(298–411°K., 1.0%)
FeS(β)	$17.40T - 4944$	(411–598°K., 0.2%)
FeS(γ)	$12.20T + 1.19 \times 10^{-3}T^2 - 2138$	(598–1468°K., 0.3%)
FeS(l)	$17.00T + 1124$	(1468–1500°K., 0.1%)
FeS_2(c)	$17.88T + 0.66 \times 10^{-3}T^2 + 3.05 \times 10^5T^{-1} - 6413$	(298–1000°K., 1.0%)

Summary

Heat content measurements of manganous sulfide, ferrous sulfide and pyrite were made between 298° and the respective temperatures, 1814, 1488 and 980°K.

Heat content relationships and a table of heat content and entropy increments are reported.

BERKELEY, CALIFORNIA RECEIVED MAY 31, 1950

[11] Kelley, Bur. Mines Bull. 476, 1940, p. 8.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Observations on the Rare Earths. LVIII.[1] Reaction between Neodymium and Ethylenediaminetetraacetate Ions in Aqueous Solution[2]

BY THERALD MOELLER AND J. CALVIN BRANTLEY[3]

Introduction

Comparatively few stable complex species derived from the tripositive rare earth metal ions are known in aqueous solution. In those cases (*e. g.*, with tartrate, citrate, etc.) where the properties of aqueous solutions are indicative of the presence of complex ions, data on stoichiometric compositions are generally lacking. Recent work has emphasized the strong complexing power of ethylenediaminetetracetic acid and has indicated the comparative ease with which systems containing it can be studied.[4-8] It seemed logical to extend studies upon this reagent to systems containing rare earth metal ions, particularly in view of qualitative observations that such systems can be made strongly alkaline without precipitation of the metal ions and are unaffected by normal precipitants for the uncomplexed cations. Reported data on such systems are limited to descriptions of the preparations of compounds of compositions $MH(C_{10}H_{12}N_2O_8)$, M = La, Nd,[6] and $Y_4(C_{10}H_{12}N_2O_8)_2 \cdot 24H_2O$.[7]

Data summarized here are for systems containing neodymium as a typical cerium earth and represent results of spectrophotometric, electrometric and electrophoretic studies.

Experimental

Materials Employed.—Standard aqueous neodymium chloride solutions were prepared[1] from a sample of neodymium oxide which contained no other rare earths. Chemically pure samples of ethylenediaminetetraacetic acid[9] were used as such or as ammonium salt solutions prepared from calculated weights of the acid by titration with aqueous ammonia to *p*H 8.0.

Apparatus.—All absorption spectra were measured with a Beckman model DU quartz spectrophotometer, following the procedure previously outlined.[1] All electrometric titrations were followed with a Beckman model G *p*H meter, the glass electrode of which had been calibrated against standard buffers. Electrophoretic migrations were studied in an H-cell with a sintered glass disc sealed into the cross arm, using platinum electrodes with a current of 0.2 ampere under a potential of 110 volts.

Results and Discussion

Absorption Spectra.—Complete spectra were obtained over the range 2500–10000 Å. for a 1:1 mixture of 0.1312 *M* neodymium chloride and 0.1312 *M* ammonium ethylenediaminetetraacetate solutions and for each of the component solutions. Absorption data were calculated in terms of *k*, the absorption coefficient[1] in the familiar Beer–Lambert relation

$$k = \frac{\log_{10} I_0/I}{cl}$$

c being the concentration in grams of neodymium per liter and *l* being 1.0 cm. Comparison of the

---

[1] For the previous communication in this series, see Moeller and Brantley, *Anal. Chem.*, **22**, 433 (1950).

[2] Presented as a portion of the Symposium on the Chemistry of the Less Familiar Elements at the 117th Meeting of the American Chemical Society, Detroit, Michigan, April, 1950.

[3] Linde Air Products Co., Research Laboratory, Tonawanda, New York.

[4] Pfeiffer and Offermann, *Ber.*, **75B**, 1 (1942).

[5] Brintzinger and Hesse, *Z. anorg. allgem. Chem.*, **249**, 113 (1942).

[6] Britzinger, Thiele and Müller, *ibid.*, **251**, 285 (1943).

[7] Brintzinger and Munkelt, *Z. anorg. Chem.*, **256**, 65 (1948).

[8] Schwarzenbach and Biedermann, *Helv. Chim. Acta*, **31**, 459 (1948).

[9] Furnished by the Alrose Chemical Company and the Bersworth Chemical Company, to which concerns the authors express their appreciation.

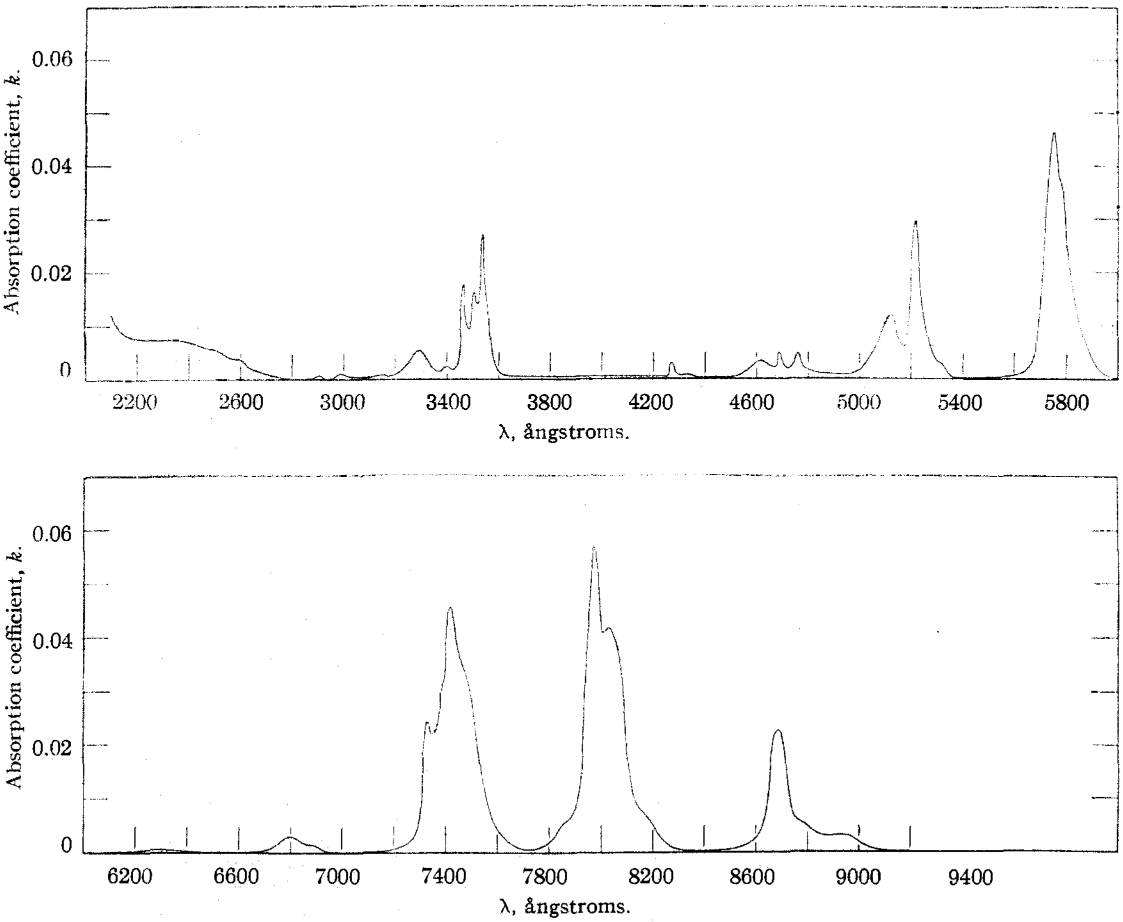

Fig. 1.—Absorption spectrum of aqueous neodymium chloride solution.

absorption spectrum of neodymium chloride solution (Fig. 1) with that of the neodymium chloride-ethylenediaminetetraacetate solution (Fig. 2) indicates not only general intensifications and bathochromic shifts of all the characteristic neodymium absorption bands in the presence of the complexing agent but also resolution of every band in the range 5100–10000 Å. into two or more bands of varying intensities and sharpnesses. This latter phenomenon is particularly striking in the 5100–6000 Å. region. Additional spectra for this region indicate that resolution of the 5218 and 5750 Å. bands of the simple neodymium ion[1] increases with increasing mole fraction[10] of ethylenediaminetetraacetate. This is apparent from the data summarized for these two bands in Table I. Except for these effects, however, the spectra in the presence and absence of ethylenediaminetetraacetate are generally similar above 2800–3000 Å. Ethylenediaminetetraacetate solutions themselves show broad absorption but only below 2800 Å.

TABLE I

WAVE LENGTHS OF NEODYMIUM ABSORPTION BANDS

Wave lengths, Å.		Wave lengths, Å.	
5220 region	5750 region	5220 region	5750 region
1.0 mole fr. Nd^{+++}		0.1 mole fr. Nd^{+++}	
5218	5750	5230	5745
0.9 mole fr. Nd^{+++}		5260	5780
5230	5755	5270	5830
	5780	5290	5860
0.5 mole fr. Nd^{+++}		5350(infl.)	5890
5210	5740		5925(infl.)
5235	5755	5370(infl.)	
5255	5790		5975(infl.)
5320	5805		
	5835		
	5860		
	5920		

Although resolution of certain complex absorption bands has been reported in the spectra of crystalline neodymium compounds and in the spectra of neodymium nitrate and bromide solutions in non-aqueous media at liquid nitrogen temperatures,[11] resolutions such as those indicated in Fig. 2 have not been described previously for aqueous neodymium salt solutions. Studies in

---

(10) Mole fraction as used in this discussion applies only to neodymium and ethylenediaminetetraacetate ions and does not take into account the quantity of solvent present.

(11) Freed and Hochanadel, *J. Chem. Phys.*, **18**, 780 (1950).

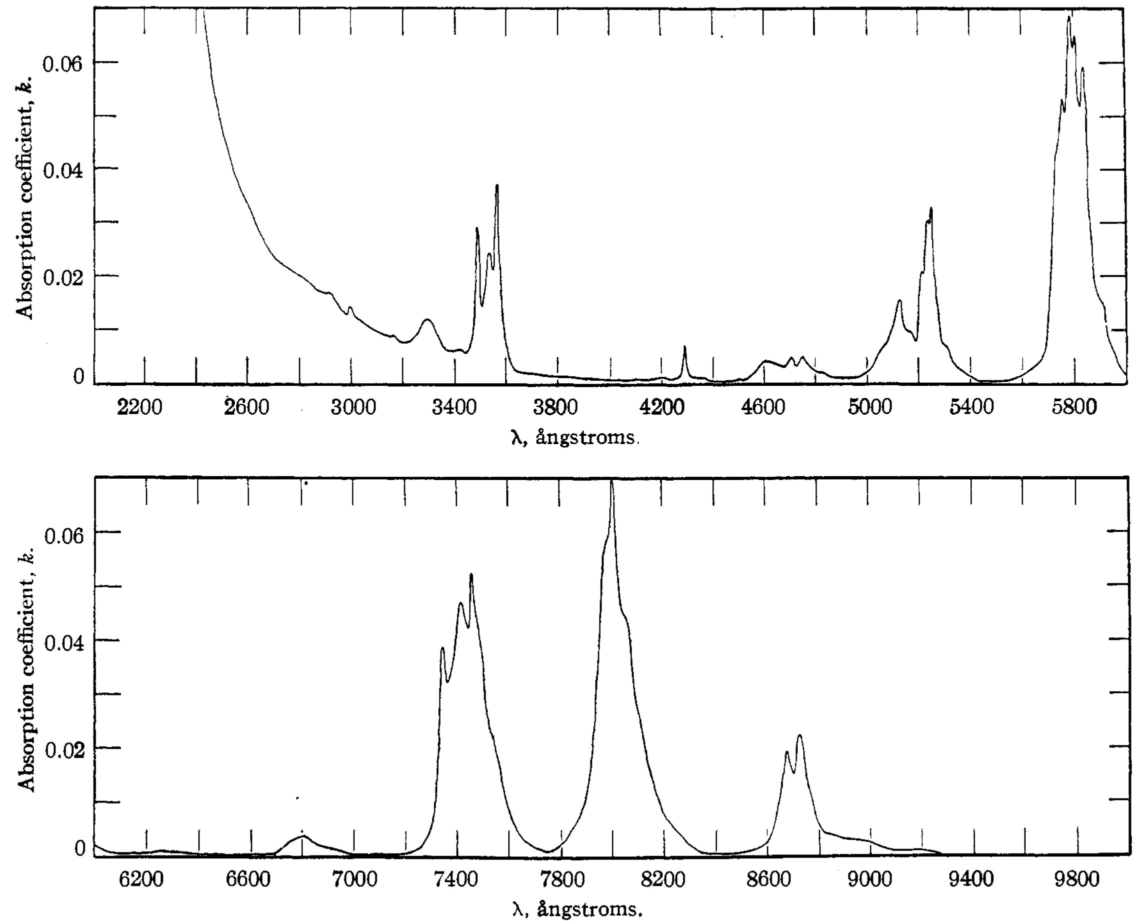

Fig. 2.—Absorption spectrum of aqueous neodymium chloride solution containing ethylenediaminetetraacetate in 1 : 1 mole ratio.

this Laboratory[12] have shown that similar effects are produced by other strongly complexing anions such as tartrate. Anions such as acetate or thiocyanate, which are weaker complexing agents, intensify absorption but do not effect band resolution.

It is reasonably well established[13] that absorption bands characteristic of the tripositive rare earth metal ions are due to forbidden transitions in 4f shells which are allowed by electric dipole effects. The natures of these bands are thus dependent upon the electrical fields imposed upon the 4f electrons. In solution such fields, as produced by the distortion of the tripositive ions by surrounding ions, are relatively weak in comparison with those existing in crystals. As a consequence, absorption bands for solutions are less intense and less complex than those characteristic of the crystalline salts. However, if a sufficiently strongly complexing anion is present, the imposed field will be intensified and absorption bands comparable in degree of resolution with those obtained for crystals may well result. The pronounced band resolutions noted in the presence of ethylenediaminetetraacetate thus indicate the imposition on the 4f electrons of fields of considerable magnitude and suggest strongly the formation of one or more complex species in solution.

That the electrons responsible for the absorption bands are not directly involved in the formation of any such complexes is apparent from the general similarities between the spectra shown in Figs. 1 and 2. These similarities preclude the use of any of the characteristic neodymium bands for evaluation of the compositions of such species by the familiar continuous variations[14] and limiting logarithms[15] procedures. Although no new absorption bands characteristic of a neodymium-containing complex have been found, solutions containing neodymium and ethylenediaminetetraacetate ions absorb much less intensely in the 2500–2600 Å. region than do those containing the organic anion but no neodymium ion. Applica-

---

[12] Brantley, Doctoral Dissertation, University of Illinois, 1949.

[13] For a comprehensive summary dealing with the origins of these spectra, see Yost, Russell and Garner, "The Rare Earth Elements and Their Compounds," John Wiley and Sons, Inc., New York, N. Y., 1947, Ch. 3.

[14] Job, *Ann. chim.*, [10] **9**, 113 (1928).

[15] Bent and French, THIS JOURNAL, **63**, 568 (1941).

tion of the method of continuous variations seemed feasible in this wave length region. Evaluation of the decrease in absorption coefficient (Δk) in this range as a function of the mole fraction of neodymium present gave the plot recorded in Fig. 3.

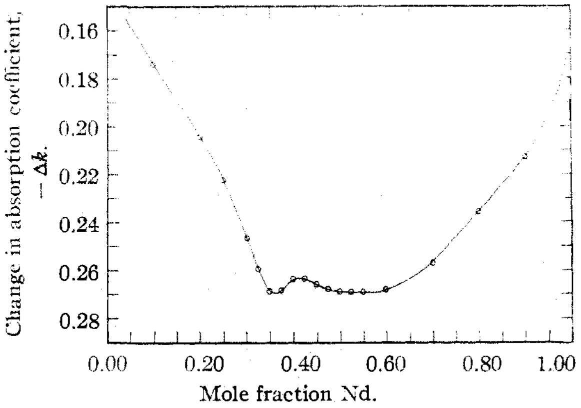

Fig. 3.—Continuous variations plot for data at 2500–2600 Å.

Although the minima in Fig. 3 at mole fractions 0.52 and 0.36 formally indicate compositions in which ethylenediaminetetraacetate and neodymium are present in mole ratios of 1:1 and 2:1, respectively, the appearance of two minima in such a curve is inconclusive. Close inspection of the curve in Fig. 3 might indicate a slight preference for a 1:1 composition, but no positive conclusions can be drawn. Absorption spectra data thus give no definite information as to the compositions of any complex species present.

Electrometric Titration.—Recorded in Fig. 4 are data obtained in the electrometric titration with standard sodium hydroxide solution of combinations of neodymium chloride and ethylenediaminetetraacetic acid in the indicated Nd:acid mole ratios and of ethylenediaminetetraacetic acid suspensions containing the equivalents of two and three moles of the acid. It is apparent that titration of ethylenediaminetetraacetic acid with alkali proceeds by the successive neutralization of two, one and one acidic hydrogens. This is in keeping with reported values of 10^{-2}, 2.1×10^{-3}, 6.9×10^{-7} and 5.5×10^{-11} for the ionization constants of the four carboxylic hydrogens.[16] At a mole ratio of one neodymium ion to one ethylenediaminetetraacetic acid, the single break in the titration curve corresponds to the neutralization of four equivalents of hydrogen ion, indicating strongly that reaction occurs in a 1:1 mole ratio. Tripositive neodymium would release only three equivalents of hydrogen ion in yielding a salt of composition $NdH(C_{10}H_{12}N_2O_8)$. However, complete dissolution of suspended material occurs only when four equivalents of hydroxyl ion are added. It appears, therefore, that the remaining carboxylic hydrogen is rendered strongly acidic and that an anionic, 1:1 neodymium complex is produced in alkaline solution. This is in agreement with the results of Brintzinger, Thiele and Müller[6] as obtained for a solid compound.

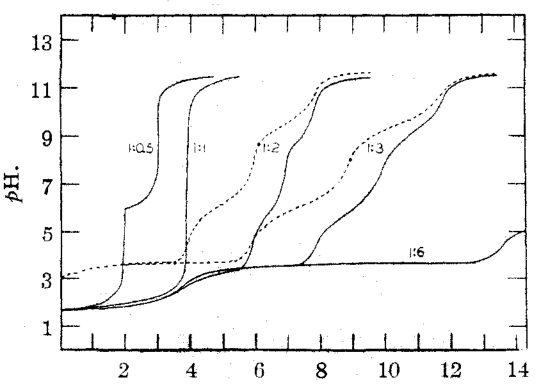

Fig. 4.—Electrometric titration data. Solid curves indicate neodymium chloride–ethylenediaminetetraacetic acid combinations at stated mole ratios as prepared in 50-ml. volumes from varying amounts of 0.1176 *M* neodymium chloride and solid ethylenediaminetetraacetic acid. Dotted curves indicate equivalent quantities of ethylenediaminetetraacetic acid alone.

Other titration data summarized in Fig. 4 support this view. Thus, the break at two equivalents of alkali in the 1:0.5 combination again corresponds to the formation of a 1:1 species and removal of the fourth hydrogen. Since there is present only sufficient acid to tie up half the neodymium, the remaining neodymium ion is precipitated as the hydrous hydroxide. The second vertical break in this curve thus corresponds to complete precipitation of uncomplexed neodymium ion. That it appears before the theoretical additional 1.5 equivalents of hydroxyl ion are added is in agreement with previous observations[17] that precipitation is always complete before a $3OH^-:1\ Nd^{+++}$ equivalence is reached. Other curves characterizing combinations in which ethylenediaminetetraacetic acid was present in excess all show breaks at four equivalents of hydroxyl ion per mole of neodymium. The remaining portions of these curves then represent titration of added acid in excess to that necessary to form a 1:1 species, as can be determined by comparing them with curves obtained for comparable quantities of the free acid alone. In no case where the acid was present in equimolar or greater quantities was there any precipitation in alkaline solution.

Electrophoretic Migrations.—The anionic nature of the neodymium–ethylenediaminetetraacetate complex in alkaline solution was confirmed by these studies. Neodymium chloride–ammonium ethylenediaminetetraacetate solutions (1:1 mole

---

(16) Schwarzenbach and Ackermann, *Helv. Chim. Acta*, **30**, 1798 (1947).

(17) Moeller and Kremers, *J. Phys. Chem.*, **48**, 395 (1944).

ratio, *p*H 8.0) were used as catholytes and equimolar potassium nitrate solutions as anolytes. After electrolysis for five hours, the anolyte and catholyte gave, respectively, positive and negative tests for neodymium with ammonium acetate and aluminon.[18] Since in the absence of the current, no physical diffusion could be detected after the same period of time, the presence of anionic neodymium was shown. Absence of a positive test for neodymium on the catholyte is not to be taken as indicating complete transfer to the anode compartment. As electrolysis is continued, the catholyte becomes more alkaline, rendering the complex too stable to permit detection of neodymium by the aluminon reagent.

Continued electrolysis caused precipitation of hydrous neodymium hydroxide on the cathode side of the sintered glass disc and gave an anolyte containing no detectable neodymium. Under these conditions, the major portion of the complexing agent was transferred to the anode compartment where, because of increased acidity, dissociation of the complex occurred. Released neodymium ions then migrated to the alkaline cathode solution where they are precipitated.

Acknowledgment.—The authors express their sincere appreciation to the Office of Naval Research for the support which rendered this investigation possible.

Summary

1. The absorption spectra of neodymium chloride solutions containing varying quantities of added ethylenediaminetetraacetate have been measured over the wave length range 2500–10,000 Å.

2. In the range 5100–10,000 Å. every neodymium absorption band is split into two or more bands. The most pronounced effects occur in the range 5100–6000 Å. where the 5218 Å. band is split into four definite bands with two additional inflections and the 5750 Å. band is split into five definite bands with two additional inflections. These effects are interpreted as indicating interactions between neodymium and ethylenediaminetetraacetate ions in solution.

3. Spectrophotometric measurements at 2500–2600 Å. suggest the presence of at least a 1:1 complex, but cannot be regarded as conclusive.

4. Electrometric titration studies indicate clearly the presence of a 1:1 complex. No evidence for any other species has been obtained.

5. Electrophoretic migration studies show the neodymium complex to be anionic in character. The complex is stable in alkaline solutions.

URBANA, ILLINOIS RECEIVED MAY 24, 1950

---

[18] Welcher, "Organic Analytical Reagents," Vol. II, D. Van Nostrand Co., Inc., New York, N. Y., 1947, p. 101.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

The Systems Cobaltous Nitrate–Water–Acetone and Cobaltous Nitrate–Water–*t*-Butyl Alcohol at 25°

BY LEONARD I. KATZIN AND JOHN R. FERRARO

High solubilities of inorganic salts in organic liquids are still generally viewed with surprise. Accumulating evidence shows that many types of salts are soluble in oxygenated organic liquids—alcohols, ketones, ethers and esters. The system uranyl nitrate–water–organic solvent was investigated for a number of organic liquids by Katzin and Sullivan.[1] They found the solubilities of uranyl nitrate on a mole % basis to be markedly greater in mixed aqueous organic systems than in pure water. Thus, although uranyl nitrate at 25° attains a concentration of 54.5% in water solution, amounting to about 5.5 mole %, it has even greater solubility in a number of water–solvent mixtures, as shown by the ternary phase studies. In some cases the concentration of uranyl nitrate may approximate 15 mole %. One or more mixed water–organic solvates could be isolated from most of these systems as stable equilibrium solid phases. As might be expected, there was a marked correlation between the tendency toward mixed solvate formation and the electron donor strength of the solvent.

To see to what extent the behavior is a function of the particular salt used and to what extent it is general, the ternary systems with water and acetone, and water and *t*-butyl alcohol, have been investigated for the salt cobaltous nitrate. The solvents chosen were those giving the least solvation (acetone) and the most solvation (*t*-butyl alcohol) in the uranyl nitrate system. Preliminary experiments had indicated that cobaltous nitrate was soluble to some extent in organic solvents.

The results to be given in detail in this paper indicate that the behavior found for the uranyl nitrate system is not limited to that salt, and is in large part a characteristic function of the solvents used. The same mixed solvates with total solvation of six were found for cobalt nitrate in the *t*-butyl alcohol system, the water component corresponding to the hydrates found in the acetone system. In the latter, the simple hydrates were formed in preference to mixed sol-

---

[1] Katzin and Sullivan, *J. Phys. Colloid Chem.*, February, 1951; Atomic Energy Commission Declassified Document No. 2537.