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THE PROPERTIES OF SUBSIDIARY VALENCE GROUPS. I. THE MOLECULAR VOLUME RELATIONSHIPS OF THE HYDRATES AND AMMINES OF SOME COBALT COMPOUNDS. II. SUBSIDIARY GROUP MOBILITY AS STUDIED BY THE HEAT DECOMPOSITION OF SOME COBALTAMMINES.

BY GEORGE L. CLARK, A. J. QUICK, AND WILLIAM D. HARKINS.

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The problem of the nature of subsidiary valence, together with the factors determining Werner's "coördination numbers," is now assuming renewed importance and interest in the light of the newer ideas on the space structure of the atom as outlined by Parson, Lewis, Born and Landè, Langmuir, and others, and on the space lattice structure of crystals as based on the researches of Laue, the Braggs, Hull, and others, together with the experimental work of Ephraim and of Biltz upon new compounds exhibiting this type of valence. The present investigation was begun 4 years ago in the endeavor to show that the interatomic and intermolecular electromagnetic fields are the largest factor in determining the stability of these compounds. The present paper treats of the closely related molecular, atomic, and group volumes. It seemed to the writers to be probable that the relative volumes of the anion, cation, and of the groups held by subsidiary valence, as they exist in the complex molecules would be of great importance in determining the stability. Ephraim[1] had already proved that the volumes of the cation and anion before entering into this combination, are of importance. The necessity for a careful study of these and other properties of subsidiary valence groups has been accentuated by the recent work of Clark and Quick[2] on the preparation of *p*-phenylene-diamine by the action of ammonia on *p*-dichloro-benzene in the presence of certain salts capable of forming ammines, thus pointing to a catalytic activation of the ammonia in the intermediate subsidiary valence stage.

The usual number of subsidiary valences is of course 6 as postulated by Werner, but it is incorrect to assign this number rigidly to all possible cases. Ephraim, as cited above, has shown that only the metals with an atomic volume less than 14 are able to form hexammines, and that the stability of the compounds containing 6 ammonia molecules and a common anion, decreases with increasing atomic volume of the cation. This is what might be expected from the general relations, since a relatively

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[1] Ephraim, *Z. physik. Chem.*, 81, 513–39 (1913); 83, 196 (1915); *Ber.*, 45, 1323 (1912).

[2] Clark and Quick, THIS JOURNAL, 42, 1033 (1920).

small atomic volume for an atom in a solid is an indication of the existence around it of a relatively intense electromagnetic field.[1]

If, as it is postulated by Ephraim, each metal atom is surrounded by 8 anion groups in the space lattice, it is reasonable to expect that when the relative volumes of the anion and cation are varied the packing will become more or less compact, and it may, therefore, be expected that, provided the group volume of the anion becomes sufficiently great, there will be the possibility of packing more than 6 ammonia groups around the cation.

Some experimental work which will be described later in this paper, and which, though it seems to be correct, is nevertheless less well verified than any of the other work of the paper on account of its sudden interruption by the war, indicates that we have been able to attach 10 ammonia groups to one cobalt atom. Certain features of the results have led us to use the term "cavity" to indicate a position in molecule, or in the space lattice of a crystal, where an extra atom may be squeezed in without adding appreciably to the total volume of the crystalline substance. It is obvious that these results may be the consequence of an entire change in the crystal and its rearrangement into a much closer state of packing.

Ephraim's work on the dissociation temperatures of the hexammines shows that with the same metal the dissociation temperature is higher for the compound with an anion of higher atomic or group volume. In his more recent work[2] he describes some octammines. Now it may be noticed that these are invariably compounds containing anions (organic aromatic radicals) which are very large compared to the metal, with the result that the "cavities" around the metal atom can actually hold *2 more* than the usual number of ammonia groups. The influence of volume thus receives a further verification.

That the addition of the 2 extra groups does not produce any remarkable change in the general characteristics of the molecules, is shown by the fact that there is little color change, thus indicating that the vibration of the more loosely bound electrons is only very slightly affected. In our own work even the addition of the 4 extra ammonia groups did not greatly change the color, though there was a definite change.

Biltz and Fetkenheur[3] have recently isolated alpha and beta, or what they consider to be *cis* and *trans* stereoisomers of the diammines of the cobaltous halides. That these are different compounds they concluded from the fact that the colors are entirely different. It will be shown in this paper that their densities are also different.

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[1] Harkins and King, "An Electromagnetic Hypothesis of the Kinetics of Heterogeneous Equilibrium, the Structure of Liquids, and Cohesion." THIS JOURNAL, 41, 970–92 (1919).

[2] Ephraim, *Ber.*, 51, 644–69 (1918).

[3] Biltz and Fetkenheur, *Z. anorg. Chem.*, 89, 97 (1914).

With all the points just outlined in view, it was considered of fundamental importance in the further study of the position and number of subsidiary valence groups and the stability of the compound to know how the groups themselves change in volume as they are packed into the space-lattice cavities of the crystal, for this would at once serve to indicate the size of the cavities, the limiting compressibility of the subsidiary groups, and the effects of both anion and cation. The purpose of this paper, therefore, is to make such an interpretation in a preliminary way from accurate measurements and comparisons of molecular volumes. It is limited to the hydrates and ammines of the chloride and sulfate of bivalent cobalt and 3 cobaltic chloride ammines for purposes of comparison. Of intrinsic value are, first, the study of the methods of preparation and the actual composition of the compounds, concerning which there is a surprisingly wide difference of opinion; and second, the specific gravity determinations. It is a reflection upon present day chemistry that the specific gravity of cobalt sulfate, for example, which is generally quoted in tables, was determined in 1845 without any refinement in method, and that several others now accepted were made with water as the liquid. A few compounds are described and specific gravities given for the first time.

Part II of this paper gives the interesting results of experiments upon the effect of heat on the cobaltammines, from which information may be gained as to the stability of the subsidiary valence unions, the constrained mobility of the groups, and the possible secondary chemical reactions when heat energy has overcome the electric and magnetic forces which enable the ammine molecule to hold together.

Experimental.

Specific Gravity Determinations.—The specific gravity determinations were carried out by means of a pycnometer having a side-arm capillary tube such as is used for the accurate determination of the densities of liquids. The stoppers were specially ground so carefully that there was no need for the use of phosphoric acid or grease as a lubricant, thereby removing any possibility of contamination. The pycnometer was repeatedly carefully standardized with freshly distilled water. The liquids used in the determinations were kerosene, xylene and toluene. They were purified by allowing them to stand over solid sodium hydroxide for several days, further dehydrated with metallic sodium, and then fractionated, the middle portion being collected. The boiling point and the specific gravity of the fraction taken at 25° and compared to water at 4° were as follows:

Liquid.	Boiling point, ° C.	Sp. gr.
Kerosene	145–180	0.78824
Toluene	106–107	0.86584
Xylene	133–134	0.86286

It might be mentioned that no vacuum correction for the pycnometer was made since the air displaced by it was always the same. The object in using 3 liquids was to avoid as far as possible any errors due to solubility of the compounds in perhaps one or another of the liquids.

The determination of the specific gravity of the various compounds to be described was based on the replacement of one of the 3 liquids by a known weight of the solid. This was weighed directly in the pycnometer, covered with the liquid and the occluded air removed by suction. The latter process was repeated after the pycnometer had been left in the thermostat for at least 30 minutes. Hygroscopic materials were introduced into the pycnometer by means of a wide funnel in a box kept desiccated. Every compound whose specific gravity was determined was passed through a 100-mesh sieve, and in the case of anhydrous salts the dehydrated salt was ground to the desired fineness, passed through the sieve and then redehydrated.

As a final check on the measurements many were repeated using instead of the pycnometer a tube 5 mm. in diameter graduated in 0.1 cc. and carefully calibrated as recommended by LeChatelier and Bogitch.[1] This was filled with the liquid, the meniscus carefully read, and then a weighed quantity of the solid introduced and the volume noted from the movement of the meniscus. Results by the pycnometric and the tube methods were entirely concordant in every case.

The results are tabulated in Table I, each single value representing an average of 3 to 6 determinations. The utmost care was exercised in every particular so that the values are probably accurate to within 0.2%. In 2 cases variations from values derived in Harvard atomic weight determinations were less than this.

Analytical Methods.—*Ammonia.* A weighed amount of the ammine was put into a small weighing bottle, dropped through a wide closed funnel into a solution of sodium hydroxide, and the liberated ammonia distilled into standard acid solution. The usual precautions were taken, including a blank test showing that the reagents were pure and that no fixed alkali was swept over.

Water.—The sample was put into a combustion tube and heated to the necessary temperature. A slow current of dry air was passed over the sample and the liberated water collected in a U-tube filled with fused calcium chloride, or, in the case of compounds containing both water and ammonia, with potassium hydroxide. Horn and Taylor[2] have shown that this latter method is entirely rigorous.

Compounds Studied.—*Anhydrous Cobaltous Chloride.* This was prepared from Kahlbaum's purest crystallized cobaltous chloride hexa-

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[1] LeChatelier and Bogitch, *Compt. rend.*, 163, 459 (1916).

[2] Horn and Taylor, *Am. Chem. J.*, 32, 256 (1904).

hydrate, by heating to 160–170° until a uniformly light blue product was obtained. It was found very advisable to conduct the dehydration in an atmosphere of dry hydrogen chloride. The preparation of the perfectly anhydrous salt presents a problem in itself. The usual recommendation for the temperature of dehydration is 140°,[1] but the salt dehydrated at this temperature always has a purplish tinge indicative of minute traces of moisture. The extremely delicate color sensitiveness to moisture shows that only the pure blue salt is really in a state of perfect dehydration, and is obtained at 160–170° in the presence of dry hydrogen chloride or hydrogen. The temperature may be raised to 400° for a short time without apparent decomposition, but at this point dark spots begin to appear. It has been found possible in this work to sublime anhydrous cobaltous chloride below 500° in a brick-lined electric oven under slight pressure of hydrogen chloride into *colorless*, but wonderfully iridescent fluffy crystals, which crumble into a pink powder in the presence of a minute amount of water vapor.

Specific gravities are as follows: in xylene, 3.360; in toluene, 3.352; in kerosene, 3.356; average, 3.356. Baxter and Coffin,[2] who made a careful determination, found practically the same value, 3.348.

Cobaltous Chloride Hexahydrate.—A pure commercial product was used. An analysis for water gave the following results:

Calc. for $CoCl_2.6H_2O$: H_2O, 45.38. Found: 45.15.

Values of the specific gravity are 1.923 in toluene, 1.925 in xylene, or 1.924 average. The only other value of this constant found in the literature and the one now generally used is 1.84, determined by Bödeker,[3] whose work has been found inaccurate in many cases.[4]

Cobaltous Chloride Dihydrate.—This compound was formed by keeping the hexahydrate over conc. sulfuric acid at 50° for 36 hours. A dark purple compound was formed giving the following analysis for water.

Calc. for $CoCl_2.2H_2O$: H_2O, 21.70. Found: 21.60.

All attempts to prepare definite intermediate hydrates between 2 and 6 failed, confirming the results of Derby and Yngve.[5] Specific gravity values are: 2.470 in kerosene, 2.485 in xylene, 2.477 average.

Cobaltous Chloride Hexammine.—This ammine was prepared in 4 different ways. The first method, following the method described by Ephraim,[6] consisted in passing dry ammonia gas over anhydrous cobaltous chloride. The first trace turned the salt deep blue, then red, then finally

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[1] Wyrouboff, *Bull. soc. chim.* [3], **5**, 462 (1871); Potilitizer, *Ber.*, **17**, 280 (1884).

[2] Baxter and Coffin, THIS JOURNAL, **28**, 1587 (1906).

[3] Bödeker, "Die Beziehung zwischen Dichte und Zusammenhang bei festenund liquiden Stoffen." Leipzig, **1860**.

[4] *Am. Chem. J.*, **31**, 228 (1904).

[5] Derby and Yngve, THIS JOURNAL, **38**, 1439 (1916).

[6] Ephraim, *Ber.*, **45**, 1323 (1912).

flesh colored. Using the perfectly dehydrated salt, a number of samples have been prepared in this way, giving practically theoretical analyses. Using, however, some of the chloride dehydrated without precautions, the ammonia content of the ammine always approximated 5.5 moles instead of 6. In the effort to raise the content the experiment was repeated at a temperature of —10°, and finally liquid ammonia was added to the salt in a Dewar bulb; but in either case the resulting product showed no appreciable increase in ammonia. Average specific gravity values of the pure hexammine prepared in the dry way are: 1.495 in toluene, 1.489 in kerosene, 1.507 in xylene, or 1.497 average in the 3 liquids.

The compound was prepared a second way by passing dry ammonia gas through a solution of anhydrous cobaltous chloride in absolute alcohol, producing first a pale red precipitate which gradually changed to the light flesh color identical in shade with that produced by the dry method. A specific gravity determination in kerosene gave 1.533.

The ammine was also prepared in the wet way, by bubbling ammonia through a saturated solution of the chloride in water. Surprisingly good results were obtained for, as the solution approached saturation perfect octahedral crystals, dark red in color, separated. These were filtered off in an atmosphere of hydrogen, washed with conc. ammonium hydroxide, then alcohol saturated with ammonia, and finally ether. The product was fairly stable in air after being dried in an atmosphere of hydrogen at slightly above room temperature. Analysis of the compound gave the following results:

Calc. for $CoCl_2.6NH_3$: Cl, 30.57; NH_3, 43.99. Found: Cl, 30.43; NH_3, 43.68.

The specific gravity of this sample is 1.506. In this connection a number of experiments were performed to ascertain whether ammonia groups will always displace water when held by subsidiary valence bonds. Dry ammonia was passed over cobaltous chloride hexahydrate and the water was absorbed by solid potassium hydroxide as it was liberated. An exceedingly unstable series of compounds is formed as the process continues, and these compounds are instantly oxidized at first contact with air. After several hours, however, all the water of hydration is replaced by ammonia and the perfectly stable hexammine is left. The greater ease with which ammonia molecules can exist as subsidiary valence groups is thus clearly demonstrated.[1]

The hexammine was finally prepared under pressure. No mention of this method could be found in the literature, although it affords a convenient process especially for cobaltous ammines which oxidize easily. By means of it the tedious process of bubbling ammonia through the solution or passing over the dry salt is eliminated, and at the same time

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[1] Ephraim and Rosenberg, *Ber.*, **51**, 130 (1918), show that the hexammine of cobaltous nitrate is very easily prepared in this way.

the yield is markedly increased and a beautifully crystalline product is obtained. The details of the method are as follows. 35 g. of hydrated chloride, 50 cc. of conc. ammonium hydroxide, and 10 cc. of alcohol were put into a pressure flask and heated in a bath of boiling water. In about an hour complete solution took place, whereupon the bath was allowed to cool very slowly. Large, well defined crystals separated. The supernatant liquid was decanted off and the crystals washed successively by decantation with conc. ammonium hydroxide, alcohol and ether. The crystals were identical in color, form and composition with those obtained by the wet method.

Cobaltous Chloride Pentammine Monohydrate.—It was found that by using the third or wet method described for the hexammine except that the solution of the chloride is first heated to boiling and then cooled down during the passage of the ammonia to —10°, a product quite different from the red octahedral crystals was obtained. It was a fine pink powder which gave the following analysis:

Calc. for $CoCl_2.5NH_3.1H_2O$: Co, 25.26; Cl, 30.31; NH_3, 36.60; H_2O, 7.73. Found: Co, 25.24; Cl, 30.39; NH_3, 36.51; H_2O, 7.55.

The cobalt in this case was determined by electrolysis as metallic cobalt from a solution made alkaline with ammonium hydroxide and containing 4 times the weight of cobalt of ammonium chloride. It is doubtful whether this is as definite a compound as the hexammine, since other samples gave a somewhat higher ammonia and lower water content. That the compound differs from the hexammine, however, is shown by the difference in their hydrolysis by water. The hexammine is completely decomposed, forming a precipitate of cobaltous hydroxide and a clear supernatant solution of ammonium chloride. This compound, however, produces a green precipitate containing about 6 moles of hydroxide to one of cobaltous chloride, and a red supernatant liquid from which separated, after 4 weeks spontaneous evaporation *in vacuo*, red octahedral crystals having the approximate composition, $CoCl_2.12NH_4Cl.8NH_3$. Hydrolysis therefore, would seem to proceed according to the following equations.

$$CoCl_2.6NH_3 + 2H_2O \longrightarrow Co(OH)_2 + 2NH_4Cl + 4NH_3;$$

$$CoCl_2.5NH_3.1H_2O + 4H_2O \longrightarrow CoCl_2.6Co(OH)_2 + 20NH_3 + CoCl_2.12NH_4Cl.8NH_3.$$

This compound also has a higher specific gravity, 1.559 in kerosene.

Cobaltous Chloride Pentammine.—Only 5 molecules of ammonia combine when the gas is conducted into a *boiling* solution of the chloride in absolute alcohol. A pale yellowish-pink colored ammine which gave the following analysis for ammonia results:

Calc. for $CoCl_2.5NH_3.NH_3$, 39.60. Found: 39.78.

The average specific gravity of this compound was found to be 1.580.

Cobaltous Chloride Tetrammine.—This was prepared in 2 entirely different ways. By keeping the hexammine prepared in the dry way over conc. sulfuric acid at 50° for 36 hours a light pink-colored product was formed giving an almost exact analysis for the tetrammine, and having a specific gravity of 1.593 in xylene. The same result is accomplished by subjecting the hexammine to continued evacuation over acid at room temperature. The loss of ammonia seems to proceed gradually and quite slowly, but after the tetrammine is reached no further loss is noted.

The other method consisted in heating cobaltous chloride pentammine monohydrate in a closed vessel at 150° in the presence of potassium hydroxide and allowing the dry ammonia gas to be reabsorbed. By doing this ammonium hydroxide (one NH_3 and the one H_2O) failed to recombine. The compound was a very pale pink in oclor and could be melted to a dark blue liquid. The following remarkable analysis was obtained:

Calc. for $CoCl_2.4NH_3$: Co, 29.58; Cl, 35.80; NH_3, 34.40. Found: Co, 29.68; Cl, 35.82; NH_3,34.31.

The only direct method recorded is by H. Rose[1] by passing dry ammonia gas over anhydrous cobalt chloride giving a blue compound. Bersch[2] later showed that the hexammine was formed instead.

When dry ammonia gas was passed through a cold solution of cobalt chloride in amyl alcohol a compound containing 38.53% ammonia was obtained, corresponding to 4.79 moles of ammonia. Curtis and Burns,[3] working under similar conditions, obtained a pale red ammine whose composition corresponded to the formula $CoCl_2.3NH_3$, and considered by Biltz and Fetkenheur[4] to be a mixture of the hexammine and the diammine which they obtained by heating the hexammine above 130°. It has been found impossible in the work of this paper to prepare any compound corresponding to a triammine, which must indicate that the solution with which Curtis and Burns worked was not completely saturated with ammonia. Experiments which need not here be detailed have been performed with amyl alcohol solutions at temperatures in 5° intervals from —10 to 125°. The tendency is for the formation of ammines and mixtures of ammines containing between 5 and 6 molecules of ammonia at temperatures below the boiling point irrespective of the method of preparation. Acetone and ethyl alcohol solutions are exactly analogous, so that the temperature of the experiment is the determining factor and not the chemical nature of the solvent in which the ammines are insoluble.

[1] Rose, *Pogg. Ann.*, **20**, 151 (1830).

[2] Bersch, *Ber. Wien. Akad.* [2], **56**, 729.

[3] Curtis and Burns, THIS JOURNAL, **39**, 33 (1917).

[4] Biltz and Fetkenheur, *Z. anorg. Chem.*, **97**, 133 (1914).

Cobaltous Chloride Diammine.—When ammonia is passed through a *boiling* solution of the anhydrous chloride in pure anhydrous amyl alcohol a distinctly pink colored compound was precipitated containing 20.74% ammonia, while 20.774% is the calculated value for the diammine. The alcohol was carefully dehydrated by allowing it to stand over solid sodium hydroxide and fractionating. The specific gravity of the diammine was 2.095 in both xylene and toluene. Two methods for the preparation of the diammines are to be found in the earlier literature: a light blue compound from heating the hexammine to 120°,[1] and a dark blue one[2] by precipitation with ammonia from acetone solution. Great interest is attached to this compound, however, by a recent isolation by Biltz and Fetkenheur[3] of 2 isomeric diammines. In order to obtain these the method was followed exactly. The pink α or *cis*-diammine was prepared by heating the pure hexammine rapidly between 152° and 175°, and was identical with the one prepared in boiling amyl alcohol solution; the blue β, or *trans*-diammine was obtained by heating the hexammine *in vacuo* at 65°. The following analyses indicate the purity of the isomers,

Calc. for $2NH_3$: NH_3, 20.74. Found: α, 20.82; β, 20.75.

The specific gravities have not been heretofore determined and are of course of fundamental importance. The values are, α, 2.097 and β, 2.073, in xylene.

Cobaltic Chloride Pentammine (Chloro-pentammine).—This compound was prepared for very special work at the University of Chicago and was obtained from there. The following analysis shows its purity,

Calc. for $CoCl_3.5NH_3$: NH_3, 33.95. Found: 34.00.

The specific gravity was 1.809 in xylene and 1.829 in toluene, or 1.819 average.

Aquo-pentammine Cobaltic Chloride.—The compound was prepared from the corresponding oxalate according to the directions given in Biltz' "Laboratory Methods of Inorganic Chemistry," and twice recrystallized. The specific gravity was 1.774 in xylene and 1.778 in toluene, or 1.776 average.

Cobaltic chloride hexammine was also prepared according to Biltz and purified by several recrystallizations. Specific gravity, 1.740 in xylene; 1.748 in toluene; 1.744 average.

Cobaltous Sulfate Anhydrous.—A current of dry air was passed over the hydrated salt kept at 280° for 4 hours. At the end the product was perfectly anhydrous and had a light lavender color. Different samples gave the following specific gravities: 3.717 and 3.705 in xylene, and 3.707 in kerosene, or an average of 3.710. The value of this constant

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[1] F. Rose, "Unters. uber ammoniak Kobaltverb.," 1871, p. 26.

[2] Naumann, *Ber.*, **37**, 4334 (1904).

[3] *Z. anorg. Chem.*, **89**, 97 (1918).

quoted in tables was determined in 1845 by Joule and Playfair,[1] who obtained 3.531.

Cobaltous Sulfate Heptahydrate.—A pure commercial product was carefully recrystallized from water and the crystals thoroughly dried. An analysis for water showed 44.95%, while the calculated value for the heptahydrate is 44.83. Specific gravities were 1.955 in toluene, 1.942 in kerosene, or 1.948 average.

Cobaltous Sulfate Hexahydrate.—By keeping the heptahydrate in an air-bath at 45° for several hours, a compound containing 40.80% water was obtained, corresponding to the hexahydrate which should analyze 41.06. The specific gravity was 2.029 in toluene.

Cobaltous Sulfate Tetrahydrate.—This was made by placing the heptahydrate over conc. sulfuric acid for 48 hours at 50°. One sample was found to contain 31.80% of water, while the calculated value for the tetrahydrate is 31.72. Two different samples gave specific gravities of 2.366 and 2.370 in xylene, for an average of 2.368.

Cobaltous Sulfate Pentammine.—In at least 15 trials in passing dry ammonia over dehydrated cobaltous sulfate, it was found impossible to prepare the hexammine of this salt, but instead always the pentammine, a light, fluffy, pink powder, was obtained, contrary to the findings of Ephraim.[2] One sample gave the following representative analysis for ammonia.

Calc. for $5NH_3$: 35.41. Found: 35.52

At —18° an ammine containing 5.2 moles of ammonia was formed. The specific gravity of the purest pentammine was 1.692 in kerosene and 1.715 in xylene, an average of 1.703.

Cobaltous Sulfate Tetrammine Dihydrate.—This compound was prepared for the first time by passing ammonia gas through a hot concentrated solution of the sulfate. By allowing the solution to cool slowly as it approached saturation, red crystals separated out, which were washed by decantation with conc. ammonium hydroxide, alcohol and ether. They are stable when dry but oxidized rapidly when dry, hence the drying and washing were done out of contact of air. The compound undergoes no change when submitted to reduced pressure for a short time, and is not decomposed when heated at 50° for 25 hours. Analysis gave the following results:

Calc. for $CoSO_4.4NH_3.2H_2O$: SO_4, 37.06; NH_3, 26.25; H_2O, 13.90. Found: SO_4, 36.85; NH_3, 26.38; H_2O, 13.20.

The compound may also be prepared by the pressure method already described, by heating together 20 g. of hydrated sulfate, 40 cc. of conc. ammonium hydroxide and 10 cc. of alcohol in the pressure flask. The

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[1] Joule and Playfair, *Chem. Soc. Memoirs*, **2**, 401 (1845).

[2] Ephraim, *Z. physik. Chem.*, **83**, 196 (1915).

average specific gravities were 1.808 and 1.807 in xylene, and 1.797 in toluene.

Discussion.

In the table are listed for each compound the specific gravity as experimentally determined in xylene, toluene and kerosene, the molecular volume, the apparent volume of the groups held by subsidiary valence, and the percentage compression of these groups from the volume in the free state at the same temperature. The latter two columns are not to be construed directly as the volume of the cavities in the space lattice of the crystal, since not only the free volume but also the electrical and magnetic stray fields of anion, cation and subsidiary group will determine

Table I.—Volume Relations of Complex Cobalt Compounds.

(Note that the atomic and group volumes given below are *apparent* volumes only. Thus the volume of the ammonia is calculated on the basis of the assumption that in the complex compounds the cobalt and chlorine have the same volume as in pure cobaltous chloride. This assumption should be kept in mind in considering the discussion presented in the paper.)

Compound.	Specific gravity at 25°.				Mol. vol.	Apparent vol. subsidiary group.	% compression.
	Xylene.	Toluene.	Kerosene.	Av.			
NH_3	.....	.....	.....	.....	28.416	....	.....
H_2O	.....	.....	.....	.....	18.069	....	.....
$CoCl_2$ anhyd.	3.360	3.352	.....	3.356	38.70	(Co, 6.77 Cl_2, 50.104)	31.95
$CoCl_2.6H_2O$	1.925	1.923	.....	1.924	123.69	H_2O, 14.165	21.40
$CoCl_2.2H_2O$	2.485	.....	2.470	2.477	66.97	H_2O, 14.25	20.91
$CoCl_2.6NH_3$	1.507	1.459	1.489	1.497	154.01	NH_3, 19.33	31.97
	1.506	.....	1.533	.....	......	....	.....
$CoCl_2.5NH_3.1H_2O$	.....	.....	1.559	1.559	149.50	NH_3, 19.29	32.12
	.....	.....	.....	.....	......	H_2O, 14.30	20.69
$CoCl_2.5NH_3$	.....	1.575	1.585	1.580	136.20	NH_3, 19.50	31.37
$CoCl_2.4NH_3$	1.593	1.594	.....	1.593	126.84	NH_3, 20.11	29.23
$CoCl_2.2NH_3$	(alpha)	.....	.....	.....	......	....	.....
	2.095	2.095	.....	2.095	78.25	NH_3, 19.77	30.43
	2.097	.....	.....	.....	......	....	.....
$CoCl_2.2NH_3$ (beta)	2.073	.....	.....	2.073	78.25	NH_3, 20.19	28.95
$CoCl_3$	.....	.....	.....	2.940	56.24	....	.....
$CoCl_3.6NH_3$	1.740	1.748	.....	1.744	153.37	NH_3, 16.09	43.37
$CoCl_3.5NH_3.1H_2O$	1.774	1.778	.....	1.776	151.29	NH_3, 16.20	42.86
	.....	.....	.....	.....	......	H_2O, 14.05	22.24
$CoCl_3.5NH_3$	1.809	1.829	.....	1.819	137.69	NH_3, 16.29	42.67
$CoSO_4$ anhyd.	3.717	.....	3.707	3.710	41.78	....	.....
	3.705	.....	.....	.....	......	....	.....
$CoSO_4.7H_2O$	.....	1.955	1.942	1.948	144.34	H_2O, 14.65	18.74
$CoSO_4.6H_2O$	.....	2.029	.....	2.029	129.67	H_2O, 14.65	18.74
$CoSO_4.4H_2O$	2.366	.....	.....	.....	......	....	.....
	2.370	.....	.....	2.368	95.90	H_2O, 13.53	24.90
$CoSO_4.5NH_3$	1.715	.....	1.692	1.703	141.03	NH_3, 19.85	30.14
$CoSO_4.2H_2O.4NH_3$	1.808	.....	.....	.....	......	NH_3, 19.10	32.77
	1.807	1.797	.....	1.804	143.67	H_2O, 13.49	25.28

what the packing in the entire molecule will be. Thus cobaltous chloride forms a hexahydrate and a hexammine, and in both cases the subsidiary forces of the cobalt atom seem completely satisfied, though some recent as yet incompletely verified work by one of the authors indicates that under very special conditions more than 6 ammonia groups may be held. The table shows that the relative volumes of water and ammonia are in the ration 14.265 to 19.33. In both cases the substituent groups must occupy relatively the same positions or cavities in the lattice; but the higher stray field of the water as measured by its higher dielectric apparently compensates for its smaller volume.

Considering the ammines of cobaltous chloride it is evident that the ammonia groups increase in volume passing down from the hexammine, assuming that the volume of the nucleus bound by primary valence forces remains constant. The 2 diammines present an interesting difference in accordance with the view either that they are *cis-* and *trans-* isomers or that their crystal form is different. The former has ammonia groups, each occupying a smaller volume than in the tetrammine, while the latter *trans-*, *β-*, or blue form follows the regular order of increase in volume of the substituent group with decrease in number.

Comparing the influence of bi- and trivalent cobalt upon the molecular volumes of the subsidiary groups, it is at once apparent that ammonia groups occupy volumes 10% smaller in the cobalt*ic* than in the cobalt*ous* ammines. The values for the former may be somewhat less accurate than for the bivalent cobalt compounds because of the larger possible error in the molecular volume of the cobaltic chloride nucleus. Even with this greater compression, however, the cobaltic ammines are more stable, as is to be expected from the much greater strength of the stray fields which give the subsidiary valence unions. It is of interest to note that in aquopentammine cobaltic chloride, the water molecule occupies a volume not greatly different from that in the cobaltous compound, and pointing to the greater susceptibility of the ammonia molecule to compression.

In the cobaltous sulfate series the relationships are somewhat different for the water molecules. These occupy the same volume exactly in both the hepta- and the hexa-hydrate, showing that the addition of the seventh molecule, which must be closely connected with the sulfate group, has no effect upon the symmetrically arranged 6. The tetrahydrate and the tetrammine dihydrate are somewhat anomalous in that the water molecules occupy less volume than the hexahydrate shows. It is quite probable that 2 of the groups occupy considerably greater volume than the other 2, whose contraction may be occasioned by the greater concentration of stray field between the sulfate group and the cobalt atom. Ammonia groups in this series are entirely comparable to their properties in the chloride; hence the tendency for the sulfate group to combine with water, aside from the usual subsidiary grouping about the cobalt atom, must be taken to explain the peculiarities in the relationships of the water molecules. A number of other relationships in the table need not be specifically pointed out here.

Preparation and Properties of Cobaltous Decammine Chloride.

Cobaltous Decammine Chloride was prepared *twice* from cobaltous chloride prepared with great care according to the method already described. One preparation was made at the University of Chicago, and the other at the University of Arizona, the preparation being made in both cases by Clark. *Three* careful and agreeing analyses were made of which 2 are given below.

	Second preparation.	First preparation.	Calc. value.
NH_3	0.5662	0.5661	0.5673
Co	0.1955	0.1966	0.1964
Cl	0.2370	0.2358	0.2362

It is remarkable that no attempt to prepare this compound has proved successful except when the original sample of cobaltous chloride, Kahlbaum's purest grade, has been used, though about 10 such attempts have been made. The compound was prepared by passing ammonia over cobaltous chloride, which is nearly colorless. In about one hour, when the layer of the powdered salt is about $^3/_{16}$ inch thick, the salt is completely changed to the hexammine. During the greater part of this period, and in the middle of the period, it was found that the ammonia adds on at an entirely constant rate. Thus in one experiment carried out in a large box containing ammonia, with the cobaltous chloride spread in a layer of about the above thickness on a watch glass, it was found that the period during which the salt absorbed 10 mg. of ammonia gas determined on a sensitive Troemner balance, gave the period of 60 seconds as accurately as it could be determined by means of a stop watch. The hexammine thus formed is almost colorless, but with a slight flesh tinge.

If no more ammonia is taken up this color remains constant, but if the ammonia addition is to go on to the decammine stage, the color begins to change slightly after many hours, and at the end of a week or more has changed gradually over to a brown. An analysis of this brown powder taken directly from the apparatus showed the presence of about 10.5 to 11 molecules of ammonia, but it was obvious that the powder held some absorbed and adsorbed gas not united chemically. On putting some of the powder in a tube and making a connection to a high vacuum for only about one minute, the compound gave the analyses listed above.

The evidence that such a compound was formed was as follows: (1) it was prepared twice with 3 analyses, together with several other analyses showing more ammonia when the ammonia caught in the powder was not removed; (2) the color change; (3) the vapor-pressure curve lies very much higher than that of the hexammine; (4) the density is altogether different; (5) on standing the compound gradually loses its brown color and changes over to the lighter color of the hexammine. The density was found to be 1.71, the molecular volume, 175.6 cu. cm., the volume of the combined ammonia was thus reduced in a very remarkable way to 13. Only 2 density determinations were made, and although they agreed perfectly, it cannot be said that this density work has been so carefully checked as the other work, since it was interrupted by the war, and now none of the compound is available for the determinations.

This compound is evidently very difficult to prepare, as the conditions for its formation have not yet been discovered. Two experiments by Harkins and about 10 by Clark, using new samples of cobaltous chloride, have proved unsuccessful, and it was evident from the original experiments that the quantity of moisture present had to be very carefully controlled.

Part II. The Effect of Heat on Cobaltous and Cobaltic Ammines.

Just as it is possible to drive water from the crystalline hydrates of the cobaltous salts without secondary reactions, so ammonia may be removed from the ammines by heat leaving the anhydrous salt, providing that care be exercised and the temperature not raised too high. The diammine, for example, is prepared from the hexammine by heating to 150° and the last 2 molecules of ammonia may be removed below 200°, though the diammine may be made to melt without decomposition. If higher temperatures are used, however, ammonium chloride is sublimed from the compound as oxidation to cobaltic oxide takes place. Even when 2 different species of groups are held by the same cobalt atom by the subsidiary valence forces—water and ammonia, for example—the effect of heat is merely to remove ammonium hydroxide without disturbing the relationship of the atoms held by primary valence forces. Thus although the ammonia groups are compressed by about $^1/_3$ of their free volume when ammines are formed (a fact which may account in large measure for the greater activity and the catalytic action of the salt in acting merely as a "compressor" and surface for adsorption) still the expansion of the groups and the ultimate liberation is not sufficient to disrupt the entire molecule, unless secondary reactions such as oxidation by the air are made possible.

On the other hand, heat has a large effect upon salts containing a central atom as easily reducible as the cobalt atom when in its higher valence. It has already been shown that ammonia groups are compressed to perhaps 10% greater amount in the cobaltic ammines than in the corresponding cobaltous compounds, and it would be expected that the cobaltic compounds would be more stable. Experiments were performed on 3 of the cobaltic ammines, the hexammine in which the effect of only one species of subsidiary group could be noted, mononitro-pentammine cobaltic chloride with 2 species, and trinitro-triammine cobalt with 2 species and without the uusal effect of an anion of an electrolyte. From none of these is it possible to remove ammonia alone without effect upon the rest of the molecule.

From the hexammine cobaltic chloride evolution of ammonia began at 173° to a slight extent, and a sublimate of ammonium chloride was apparent at 181°. The first step consisted in the formation of chloropentammine cobaltic chloride, $[Co(NH_3)_5Cl]Cl_2$, agreeing with the work of Biltz.[1] Rapid increase in vapor pressure began at 220°, and at 228° it was 1054 mm. The original orange-red salt was now dark blue. Reabsorption of ammonia reduced the pressure by 392 mm. and caused the residue to become dark maroon in color. The residual gas, 101 cc., was collected above mercury and all but 6 cc. (which later proved to be nitrogen) dissolved in water showing it to be largely ammonia. The pump was now attached to the vessel containing the solid residue, and the gas withdrawn at 260° for one hour. The residue light blue in color and easily dissolved in water to give a wine colored solution. Upon analysis it proved to be cobaltous chloride together with ammonium chloride in the ration 1 : 2, or $CoCl_2.2NH_4Cl$, though this ratio was undoubtedly accidental inasmuch as a considerable quantity of ammonium chloride had sublimed. This experiment was carried on throughout, out of contact with air and represents the spontaneous decomposition of the molecule with heat according to the following equation.

$$6[CoCl_3.6NH_3] \longrightarrow 6CoCl_2 + 6NH_4Cl + N_2 + 28NH_3.$$

This behavior is much more easily explained upon the basis of Werner's structure than Friend's cyclic structure.[2]

Proceeding in similar fashion with mononitro-pentammine cobaltic chloride, it was found that the gas exerted noticeable pressure at 100° and rapid evolution began at 210°. The gas liberated below 248° was drawn off above mercury and analyzed, showing a total of 87.1 cc., composed of nitrogen 70.3 cc., and ammonia 16.8 cc. Oxygen, hydrogen, nitric and nitrous oxides were tested for and found not present. Water was formed in appreciable quantities in the heating bulb, which, together with the large evolution of nitrogen, indicated the intermediate formation of ammonium nitrite. The solid residue left in the bulb was dicobalt trioxide, agreeing in all properties and giving the following analysis

Calc. for $CoSO_4$: Co, 71.08. Found: 70.96.

The mechanism of this reaction is very probably as follows.

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[1] *Z. anorg. Chem.*, 83, 177 (1913).

[2] *J. Chem. Soc.*, 109, 715 (1916).

$$Co(NH_3)_5(NO_2)Cl_2 \longrightarrow NH_3 + 2NH_4Cl + NH_4NO_2 + CoN;$$
$$NH_4NO_2 \longrightarrow N_2 + 2H_2O;$$
$$2CoN + 3H_2O \longrightarrow Co_2O_3 + 3NH_3;$$

or,

$$2Co(NH_3)_5(NO_2)Cl_2 \longrightarrow Co_2O_3 + 5NH_3 + 4NH_4Cl + 2N_2 + H_2O.$$

This case differs, therefore, from the preceding one in that the cobalt atom is not reduced, because of the interaction of 2 species of molecules both with subsidiary valence unions.

The results with trinitro-triammine cobalt are somewhat similar, but very interesting. Slight evolution of gas begins at 158°, but at 164° the decomposition takes place with almost explosive violence, forming pure nitrogen, water and cobaltic oxide, according to the following reactions.

$$2Co(NH_3)_3(NO_2)_3 \longrightarrow 2CoN + 2HNO_2 + 4NH_4NO_2;$$
$$4NH_4NO_2 \longrightarrow 4N_2 + 8H_2O;$$
$$2CoN + 2HNO_2 \longrightarrow Co_2O_3 + H_2O + 2N_2;$$

or,

$$2Co(NH_3)_3(NO_2)_3 \longrightarrow 6N_2 + 9H_2O + Co_2O_3.$$

The writers wish to express their indebtedness to the Gibbs Fund of the National Academy of Sciences for a grant of two hundred dollars made to W. D. Harkins, which was used in purchasing a very rapid vacuum apparatus, consisting of a mercury condensation pump, and a large supporting pump of the mechanical type, for use in this work.

CHICAGO, ILL., AND NASHVILLE, TENN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN.]

THE PREPARATION OF SELENIUM OXYCHLORIDE.

BY VICTOR LENHER.

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The first record in the literature that we have of selenium oxychloride is its preparation by Weber[1] in 1859, who heated together in a knee-shaped tube the vapors of selenium tetrachloride and selenium dioxide. Michaelis[2] prepared the oxychloride by the action of phosphorus pentachloride on selenium dioxide. Later, in 1889, in their work on selenic acid, Cameron and Macallan,[3] mention that selenium oxychloride is formed when common salt is distilled with selenium dioxide.

The methods used in this laboratory for the formation of selenium oxychloride may be grouped under 3 heads.

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[1] Weber, *Pogg. Ann.*, **108**, 615 (1859).

[2] Michaelis, *Ann.*, **240**, 150 (1887).

[3] Cameron and Macallan, *Chem. News*, **59**, 267 (1889).