THE PROPERTIES OF SUBSIDIARY VALENCE GROUPS. III
THE PREPARATION, PROPERTIES AND MOLECULAR VOLUME RELATIONSHIPS OF THE HYDRATES AND AMMINES OF COBALT FLUORIDE, BROMIDE, IODIDE, NITRATE, CARBONATE AND CITRATE.[1]

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In a former paper[2] in which the preparation, properties and molecular volume relationships of cobalt chloride and sulfate were considered, evi·dence was presented that the relative volumes of anion and cation in subsidiary valence compounds were of great importance in determining stability. Thus a theory, derived independently but amending and emphasizing certain of the findings of Ephraim in 25 papers,[3] was outlined for the existence of cavities in the space lattice[3] which hold the subsidiary groups and result from the packing of anion and cation in crystals. These cavities, it was pointed out, are in general larger, the greater the *difference in volume* between anion and cation, as judged by the fact that ammines are increasingly more stable in this same ratio and may actually contain more than 9 groups. It was further shown that the ammonia and water groups are compressed to the extent of 30 and 20%, respectively, of the liquid volume[5] when held by subsidiary valence forces in the space lattice cavities (40% for ammonia in *cobaltic*-ammines), and that in consequence there is apparent activation as shown by remarkable catalytic action of substances capable of forming ammines upon the preparation of *p*-phenylenediamine

[2] Clark, Quick and Harkins, THIS JOURNAL, **42**, 2483 (1920).

[3] Ephraim, *Ber.*, **45** to **54** (1913–21).

[4] The existence of cavities in certain types of space lattices has been completely confirmed by experiments, as yet unpublished, of Dr. Paul Bridgman of Harvard University.

[5] Assuming that the anhydrous salt which serves as a nucleus has essentially the same volume before and after NH_3 and H_2O are bound. As a matter of fact the NH_3 groups bound in hexammines at 25° actually occupy only $1/1200$ the volume of the same weight of gaseous ammonia at 1 atm. pressure and the same temperature. Dis·regarding liquefaction, the secondary valence binding force might, therefore, be roughly equivalent to 1200 atmospheres pressure.

from *p*-dichloro-benzene and ammonia. Finally, a comparison was made between ammines of cobalt salts in which the central atom has 2 valences. Although under ordinary conditions, in keeping with the Abegg-Bodländer rule, the *cobaltic* ammines are more stable than the *cobaltous* by virtue of the larger stray field of the atom in its higher valence, the greater compression of the ammonia groups easily explains the fact that heat disrupts the cobaltic-ammine molecule, while it has no effect on the primary valence forces in cobaltous-ammines, serving merely to permit removal of the ammonia groups from the "cavities."

The present paper is concerned chiefly with the accumulation of further data bearing upon the fundamental theoretical points already presented, and enabling some new and interesting comparisons to be made. Most of the ammines and ammino-hydrates to be described are entirely new. The general methods of procedure as regards precautions in preparation, analysis and determinations to the highest possible degree of accuracy of the specific gravities, were the same as in the preceding paper of this series on cobalt chloride and sulfate. Especial attention was given to the determination of the specific gravities of ammines, inasmuch as numerous statements are to be found in the literature that it is impossible to carry out such exact measurements on unstable compounds when evacuation is necessary to remove adsorbed air. In an extended study, the numerical results of which will be published later, it was found that by proportioning the evacuation pressure, to which the pycnometer containing solid and liquid is subjected, to the stability of the compound, and varying the time, adsorbed gases can be removed without sensible loss of ammonia chemically combined, as shown by subsequent analysis. The temperature was of course kept as low as the freezing point of the liquid used would permit, and only small quantities of the solid in a thin layer used. Thus a reduction of pressure to 50 mm. at the freezing point of benzene easily allows the removal of adsorbed gas from cobalt or nickel halide hexammines which have a vapor pressure of ammonia reaching 760 mm. above 150°. Lower ammines are handled as easily as stable hydrates. With very unstable ammines such as lithium chloride tetrammine, which has an atmospheric vapor pressure of ammonia at 15°, either very slight intermittent suction at low temperatures may be used, or recourse taken to the LeChatelier method of introducing a small smooth crystal into a small-bore graduated tube and measuring the change in volume of the contained liquid. In this particular case, however, accurate work is simplified by the fact that the ammine is partially melted, so that a liquid already bathes the crystals and evacuation is unnecessary. Another promising method where benzene is used consists in sweeping a stream of its vapor over the solid before immersing in the liquid. A surprisingly complete removal of adsorbed gases is possible. In all cases of specific gravities reported in this

paper, the values are averages of several determinations, checked by analysis of the ammine after spontaneous evaporation of the benzene.

In studies on the hydrates and ammines of cobaltous fluoride, chloride, bromide, iodide, nitrate, carbonate and citrate it has been the attempt to follow the speed with which dry ammonia gas is absorbed by the anhydrous salt. For this work a balance was adjusted so that one of the pans swung by a fine silk thread in a chamber which was tight except for the small opening through which the thread passed. The anhydrous salt was placed upon the pan in the chamber, and perfectly dry ammonia conducted in a constant stream into the chamber. The speed of ammonia combination and the composition of the ammine could then be definitely followed by adjusting weights upon the other pan of the balance. Special precautions were taken to exclude traces of moisture, particularly in the work with cobalt fluoride. Soda lime, potassium hydroxide and metallic sodium were kept in the glass vessel enclosing the balance pan, and the stream of ammonia, dried by passing through towers of the above substances, was kept flowing rapidly enough to prevent entrance of air through the opening into the balance case, which was in turn kept closed and dry.

Experimental.

Cobaltous Fluoride Trihydrate.—This compound was prepared by the action of hydrofluoric acid on an imported cobaltous carbonate. Rapid concentration of the solution in a platinum dish on the water-bath and stirring during the process of concentration caused the formation of small crystals. A crust which adhered tenaciously to the sides of the dish was discarded. The rose-red crystals obtained in this way were washed with absolute alcohol and ether and dried. Owing to the presence of sodium carbonate in the cobaltous carbonate the salt contained a small amount of sodium fluoride. Considerable difficulty was experienced in the analysis for water, as the salt is completely dehydrated only at a temperature of 300° in a stream of nitrogen. Analysis for cobalt and water gave the following results.

Analyses. Calc. for $CoF_2.3H_2O$: Co, 39.05; H_2O, 35.79. Found: Co, 38.78 (av. 4 detns.); H_2O, 35.64 (av. 5 detns.).

The specific gravity of cobaltous fluoride trihydrate is 2.583.

No reference to a trihydrate is to be found in the literature, but the corresponding nickelous fluoride trihydrate has been prepared.[6] Cobaltous fluoride dihydrate and a hydrated acid salt[7] have been prepared and described. Poulenc[8] prepared cobaltous fluoride in the anhydrous condition by heating to fusion the chloride with an excess of ammonium fluoride, forming the double fluoride, $CoF_2.2NH_4F$, which on further heating in an atmosphere of an inert gas yielded the anhydrous salt in an amorphous condition. Several attempts to prepare the anhydrous salt by this method were without success, the oxide being formed instead.

[6] Clarke, *Am. J. Sci.*, **13**, 291 (1877).

[7] Bohm, *Z. anorg. Chem.*, **43**, 326 (1905). Edmister and Cooper, THIS JOURNAL, **42**, 2419 (1920).

[8] Poulenc, *Compt. rend.*, **114**, 1426 (1892).

Cobaltous Fluoride Hexammine.—This ammine was prepared for the first time, by passing dry ammonia gas over the anhydrous salt placed on the pan of a balance as already described.

The anhydrous salt darkens within a few minutes. Forty minutes was required for the salt to take on one mole of ammonia while nearly 24 hours was required to take on the last mole, as the following table shows.

CHANGE IN COMPOSITION WITH THE TIME

Hours	Minutes	Composition	Hours	Minutes	Composition
0	0	CoF_2.	5	45	$CoF_2.4NH_3$
0	40	$CoF_2.NH_3$	10	9	$CoF_2.5NH_3$
1	44	$CoF_2.2NH_3$	23	55	$CoF_2.6NH_3$
3	21	$CoF_2.3NH_3$			

A total of 6.3 moles of ammonia were taken on by the anhydrous salt, the excess of ammonia probably being either absorbed or adsorbed or both. On standing in a dilute atmosphere of ammonia the ammine slowly lost ammonia.

The specific gravity determined in liquid petrolatum when the weight of the ammine showed it to contain 0.15% under the calculated value for NH_3 in $CoF_2.6NH_3$, is 1.744. At 25° cobaltous fluoride hexammine is a dark reddish-brown liquid, solidifying when cooled in an ice-salt freezing mixture. It is easily soluble in water without hydrolysis. Upon analysis absolutely no water was found present in the liquid.

It is of interest to note here another of the anomalies in the chemical nature of fluorine and its compounds. It might be expected that, due to the strong field around the molecule of cobaltous fluoride, the compound would tend to take on ammonia groups with greater rapidity than cobaltous chloride, but in fact this tendency is entirely offset by the greater compression which the ammonia groups must undergo to pack themselves into the space lattice cavities, so great being the compression that the crystal structure is completely broken down at ordinary temperatures, resulting in the liquid ammine. Anhydrous cobaltous chloride is changed to the hexammine on exposure to ammonia gas for one hour,[2] while nearly 24 hours is required to change the fluoride completely to a hexammine under practically the same conditions. The hexahydrate of cobaltous fluoride is not known to exist. It is not surprising then, that six ammonia groups occupying a greater volume than six water groups cannot be packed into the space lattice cavities of the crystal to form a crystalline ammine.

Cobaltous Fluoride Tri-ammine.—The equilibrium product resulting when the hexammine is allowed to stand in cool dry air is the tri-ammine, light pinkish-brown in color. Two samples lost practically the calculated amount for 3 molecules of ammonia. *Nickel fluoride tri-ammine*, pure steel-gray in color, exactly corresponds. When placed in a vacuum desiccator over sulfuric acid at 40° the tri-ammine loses ammonia continuously until the anhydrous salt remains. The hexammine and tri-ammine are therefore the only true compounds. This point is one of great interest inasmuch as all

the other halides form hexammines, di-ammines and mono-ammines (except that there is no iodide mono-ammine).

Cobaltous Bromide Hexahydrate.—This compound was prepared by treating cobaltous carbonate with hydrobromic acid of sp. gr. 1.49, and evaporating on a water-bath to the formation of a deep blue solution. The concentrated solution thus obtained when cooled in ice-cold water yielded purple-red crystals of the hexahydrate. The purest obtainable cobaltous carbonate was contaminated by sodium carbonate from which it could not be freed by repeated washing with water. Boiling water hydrolyzes cobaltous carbonate. The hexahydrate, therefore, contained a small amount of cubes of sodium bromide and rhombic prisms of the dihydrate. The former are less soluble and the latter more soluble than the hexahydrate. At least a dozen recrystallizations from water did not serve to free the salt from sodium bromide. The deliquescent crystals were dried between filter papers.

Analysis. Calc. for $CoBr_2.6H_2O$: Co, 18.04. Found: 18.68.

Anhydrous Cobaltous Bromide.—It was found that the anhydrous salt can be easily prepared by very carefully heating the hydrated salt to 150°. The hexahydrate was also completely dehydrated by allowing to stand for several weeks over conc. sulfuric acid, yielding the green cobaltous bromide.

In addition the following hydrates have been described.[9]

$CoBr_2.5.5H_2O$	rose-colored	$CoBr_2.2H_2O$	purple
$CoBr_2.5H_2O$	pink	$CoBr.H_2O$	blue
$CoBr_2.4H_2O$	reddish-violet	$CoBr_2.0.5H_2O$	(?)

It is probable that the hexahydrate when left over the green anhydrous salt until equilibrium is reached changes to the pink pentahydrate, for a pink salt obtained in this manner after several weeks standing gave the following analysis for cobalt.

Analysis. Calc. for $CoBr_2.5H_2O$: Co, 19.19. Found: 19.46.

Various ammino-hydrates, one corresponding approximately to the formula $CoBr_2.2NH_3.7H_2O$ but more likely a mixture, were prepared by saturating strong ammonium hydroxide with cobalt bromide, adding a little alcohol and allowing the solution to evaporate spontaneously to dryness.

The **hexammine** has been prepared by exposing the anhydrous bromide to dry ammonia gas,[10] and also by leading ammonia into a solution of the salt in methyl acetate. It is possible that its preparation can be effected by any one of the three other methods described in the first paper[2] of this series.

The hexammine loses ammonia on heating, changing at 120° to a blue salt of the composition $CoBr_2.2NH_3$. The α and β forms of the **di-ammine** have been prepared according to the directions of Biltz and Fetkenheur,[11] together with the mono-ammine. *An interesting new method for the preparation of the mono-ammines* of cobalt chloride, not described in the former paper, and cobalt bromide was developed. This consisted in heating at 230° in a closed tube an intimate mixture of the corresponding hexammine and anhydrous salt in calculated proportions. During this heating a very distinct color change takes place, the chloride changing to a blue-violet and the bromide to a blue, and very definite mono-ammines of theoretical composition are obtained. In the case of cobaltous iodide, however, the final product is a mixture of the di-ammine and anhydrous salt, easily distinguishable under the microscope, and proving the non-existence of the mono-ammine of the iodide.

Cobaltous Iodide may be obtained in the anhydrous condition as a black metallic-

[9] Guareschi, *Atti acad. sci. Torino,* **48**, 929 (1913).

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

[11] Biltz and Fetkenheur, *Z. anorg. allgem. Chem.,* **87**, 97 (1918).

looking mass by heating cobalt in a current of iodine vapor, or by desiccation of the hydrated salt over conc. sulfuric acid *in vacuo*.[12]   It is most readily obtained by warming the finely divided metal with water and iodine.

The hexahydrate is obtained as dark red, hexagonal prisms, by evaporating and then strongly cooling the aqueous solution.   Further concentration yields the nona- hydrate which crystallizes in red, rhombic plates, which lose 3 molecules of water at 6.4°.[13]   The tetrahydrate and the dihydrate are green.

The hexammine[14] and two di-ammines[11] have been prepared.

Cobaltous Nitrate Hexahydrate.—A pure commercial product was used.   The deliquescent crystals were placed in a desiccator over the partly dehydrated salt and left until equilibrium was established, when the product is a light reddish-brown.   An analysis for cobalt shows the purity of the salt.

Analysis.   Calc. for $Co(NO_3)_2.6H_2O$: Co, 20.26.   Found: 20.29.
The specific gravity in toluene was 1.8800; in liquid petrolatum, 1.8854; av. 1.883.

Cobaltous Nitrate Dihydrate.—This was obtained by allowing the hexahydrate to stand over conc. sulfuric acid for a period of 3 months.   An analysis for cobalt gave the following result.

Analysis.   Calc. for $Co(NO_3)_2.2H_2O$: Co, 26.92.   Found: 26.91.
The specific gravity in liquid petrolatum was 2.397.

Attempts to prepare the trihydrate by melting the hexahydrate and keeping it at 70–74°[15] were unsuccessful, and instead a salt giving an analysis of 26.53% for cobalt was obtained, this value being nearly that for cobalt in the dihydrate.

Cobaltous nitrate has been obtained in the anhydrous condition by the action of nitric anhydride on the hydrated salt.[16]

A break in the solubility curve of the salt at −22° is attributed by Funk[15] to the formation of a nonahydrate.

Cobaltous Nitrate Hexammine.—This ammine was prepared in a very pure state by placing a small quantity of the hexahydrate in a tube which could be heated con- veniently in an electric oven, and passing a rapid current of dry ammonia over it.   A series of color changes takes place due to the formation of unstable intermediate compounds. The salt becomes violet at first contact with ammonia, then black, and finally assumes the original color of the hexahydrate.   The last traces of water were driven out only by alternately heating to 40° and further passing of ammonia.   Several hours were required for the preparation.[17]

The perfectly anhydrous salt is stable, but in the presence of a slight amount of moisture it gradually darkens.

The mean of two analyses for cobalt was as follows.

Analyses.   Calc. for $Co(NO_3)_2.6NH_3$: Co, 20.68.   Found: 20.68.

The specific gravity in liquid petrolatum is 1.473.

An unsuccessful attempt was made to prepare the hexammine by placing the hexahydrate on a balance pan swung in a chamber through which a current of ammonia was passed.   The water of hydration was not driven out after a period of several days. A black intermediate compound was formed of the approximate composition $Co(NO_3)_2$.-

[12] Hartley, *J. Chem. Soc.*, **27**, 501 (1874).

[13] Bolschakoff, *J. Russ. Chem. Soc.*, **30**, 386 (1898).

[14] Ephraim, *Ber.*, **46**, 3742 (1915).

[15] Funk, *Z. anorg. Chem.*, **20**, 393 (1899).

[16] Guntz and Martin, *Bull. soc. chem.*, **5**, 1004 (1909).

[17] Ephraim and Rosenberg, *Ber.*, **51**, 130 (1920), state that the hexammine is easily prepared in this way.

$6NH_3.3H_2O$. This compound was immediately hydrolyzed by water with effervescence. A rose colored compound[18] of this formula has been prepared in the crystalline state by the addition of ammonia in excess to a solution of cobaltous nitrate in the absence of air.

A similar black compound was prepared by putting into a pressure flask a saturated solution of cobalt nitrate, strong ammonium hydroxide and a little alcohol, and heating the flask for an hour in a bath of boiling water. On slowly cooling, the compound was deposited in the form of dark needles. Red needles were also deposited around the sides of the flask on longer standing, and were undoubtedly the crystalline hexa-ammoniate of Fremy.[18] They became darkened at first contact with the air. The dark needles obtained by the pressure method, when cooled to 0° while a current of dry ammonia was passed over it, yielded a compound of the probable formula $Co(NO_3)_2.6NH_3.H_2O$.

The above compounds are very unstable. Heated on the blade of a spatula in a flame, they decompose with violence, leaving the black oxide of cobalt.

On standing for 2 months at 20–25° in an open vessel, the unstable hexa-ammoniate lost ammonia and water and gave a dark green compound of the formula $Co(NO_3)_2.3NH_3.H_2O$. Analyses for cobalt and ammonia gave the following results.

Analyses. Calc. for $Co(NO_3)_2.3NH_3.H_2O$: Co, 23.4; NH_3, 20.3. Found: Co, 23.1; NH_3, 20.4.

Cobaltous Carbonate.—An imported product was used. The sample, containing a small amount of sodium carbonate, was dried for 1.5 hours at 105–110°. The specific gravity in toluene was 2.818.

In an attempt to prepare pure anhydrous cobaltous carbonate, a saturated solution of the chloride was shaken in a pressure flask with a strong solution of sodium hydrogen carbonate. The stoppered flask was allowed to stand for several days, and the salt was then washed thoroughly with water. An analysis for water showed it to be a hydrate of the formula $3CoCO_3.2H_2O$.

Analysis. Calc. for $3CoCO_3.2H_2O$: H_2O, 9.17. Found: 9.19.

A crystalline salt[19] of the same formula has been prepared. By carrying out the reaction at low temperatures the hexahydrate is formed as small crystals. At a temperature of 140° the anhydrous salt is produced as a bright red powder.[20]

Cobaltous Carbonate Tri-ammine Tetrahydrate.—Anhydrous cobalt carbonate does not take on ammonia to form an ammine when placed in an atmosphere of the gas, although nickel carbonate does. By dissolving the salt in strong ammonium hydroxide and spontaneously evaporating the solution *in vacuo*, a dark red crystalline compound was prepared of probable formula $CoCO_3.3NH_3.4H_2O$. An analysis for ammonia gave the following result.

Analyses. Calc. for $CoCO_3.3NH_3.4H_2O$: H_2O, 29.75; NH_3, 21.1. Found: H_2O, 30.0; NH_3 20.9.

The ammine is unstable, losing ammonia to form a lighter colored compound.

Cobaltous Acid Citrate Dihydrate.—A pure commercial product was used. An analysis showed it to be the dihydrate of the acid salt in which the cobalt binds 2 citrate groups.

Analysis. Calc. for $Co(C_6H_7O_7)_2.2H_2O$: Co, 12.36. Found: 12.19.

A sample dried at 80–85° in a current of air for 24 hours gave as the specific gravity of the anhydrous salt 1.851 in liquid petrolatum.

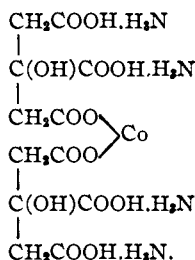**Cobaltous Citrate Tetrammine.**—This was prepared by dissolving cobalt citrate in

[18] Fremy, *Ann. chim. phys.*, **35**, 257 (1852).

[19] H. Deville, *ibid.*, **35**, 441 (1852).

[20] Betrand, *Jahrb. Miner.*, **2**, ref., 161 (1883).

strong ammonium hydroxide and evaporating spontaneously *in vacuo*. A pink and very stable crystalline ammine was produced, of the formula

$$CH_2COOH.H_3N$$
$$|$$
$$C(OH)COOH.H_3N$$
$$|$$
$$CH_2COO$$
$$\qquad\qquad >Co$$
$$CH_2COO$$
$$|$$
$$C(OH)COOH.H_3N$$
$$|$$
$$CH_2COOH.H_3N.$$

It will be seen that this compound differs from the other ammines described in this paper in that the ammonia groups have attached themselves to the carboxyl groups and therefore do not surround the cobalt atom.

Analyses for cobalt and ammonia are as follows.

Analyses. Calc. for $Co(C_6H_7O_7)_2.4NH_3$: Co, 11.62; NH_3, 13.38. Found: Co, 11.32; NH_3, 13.60.

The specific gravity in liquid petrolatum was 1.686.

It is quite apparent that in cobalt citrate there should be a larger difference between the volumes of the cation and anion than in the halides, and that this should enable combination with 6 or even more ammonia groups.[21] The citrate does form a tetrammine of great stability but no hexammine. However this is the case of an acid salt in which there are still present 4 hydrogen atoms in 4 carboxyl groups which are coördinate with and protect the cobalt atom from the exercise of its usual secondary

TABLE I

Substance	Density	Molecular vol.	Apparent volume of subsidiary group	Contraction %
KF		23.4		59.2
KCl		37.52		45.0
KBr		43.30		40.2
KI		53.16		33.3
	4.22			
CoF_2	4.43	23.6		27.5
$CoCl_2$	3.356	38.70		25.86
$CoBr_2$	4.91	44.79		26.3
CoI_2	5.68	55.04		27.3
$CoF_2.6NH_3$	1.744	114.2	NH_3: 15.4	40.8
$CoCl_2.6NH_3$	1.497	154.01	19.33	26.3
$CoBr_2.6NH_3$	1.955	164.07	19.89	23.7
$CoI_2.6NH_3$	2.36	174.6	20.10	22.1
$CoCl_2.6H_2O$	1.924	123.69	H_2O: 14.165	15.9
$CoBr_2.6H_2O$	2.46	132.69	14.65	18.58
$CoI_2.6H_2O$	2.90	145.06	15.01	11.2
$Co(NO_3)_2.6H_2O$	1.883	154.61		
$Co(NO_3)_2.6NH_3$	1.473	193.49		
$Co(NO_3)_2$	2.49 (calc.)	73.5 (calc.)		

[21] One of the authors has just prepared for the first time the compounds [Co(NH_3)_8]_3[Co(NO_2)_6]_2 and [Co(NH_3)_8] [Co(NO_2)_4(NH_3)_2]_2, verifying Ephraim's experimental work showing that with anions of very large volume, octammines may be formed.

valence forces.   There are several facts which point to the conclusion that in the tetram-mine the ammonia groups instead of being held by the cobalt atom are actually combined with the 4 carboxyl groups in which the hydrogen atoms have not been replaced by metal: (1) the great stability of the ammine; (2) the impossibility of removing ammonia by heat without complete decomposition of the compound; (3) the absolute absence of hydrolysis when water is added, as contrasted with the very rapid hydrolysis usual for the ammines; (4) the inability of dry ammonia to act upon the citrate, and the con-sequent preparation by the spontaneous evaporation of the solution in strong ammonium hydroxide; and (5) the much larger contraction of the ammonia groups (the volume of each is only 16) than is the case when they do not enter into the formation of ammonium ions.

Discussion.

In considering the relationships between the cobalt compounds dis-cussed in this and the preceding paper[2] the most interesting possibilities
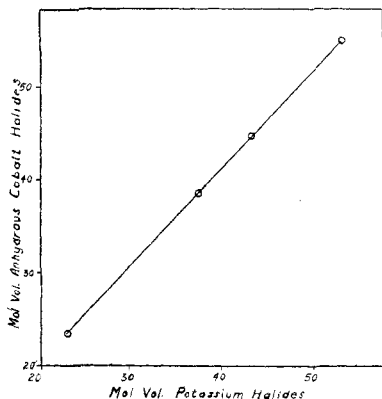

Fig. 1.

obviously are to be found in the 4 co-baltous halides and their hydrates and ammines.   The comparison is simplified inasmuch as with a constant metal cation are combined 4 anionic atoms which are as nearly perfectly graduated as possible from fluoride to iodide with respect to atomic volume and chemical activity or stray field of similar type. This is very beautifully shown in Fig. 1, in which the molecular volumes of the 4 potassium halides are plotted against those of the corresponding anhydrous cobalt halides.   A perfectly straight line

is the result—a constant relation between the halogen atoms in com-pounds which could scarcely be anticipated.   This method, while in a general way related to some suggestions by Fajans and Grimm,[22] offers splendid possibilities for the study of the halides of all metals,[23] allows the determination of molecular volumes and specific gravities once the slope of the line is established by known values for *two* of the halides of any particular metal, affords a check upon data on densities, is at once a criterion for the appearance of any secondary and abnormal effects peculiar to a metal and its combination with any one of the halo-

[22] Fajans and Grimm, Z. *Physik,* **2,** 299 (1920).

[23] Since this paper was written in original form a paper by Biltz, Z. *anorg. allgem. Chem.,* 115, 241 (1921), has been discovered which extends the same procedure to a large number of halides besides those of cobalt and to organic derivatives, fully confirming the linearity of halogen properties.   In our own work the molecular volumes of the potassium halides were used because of the undoubted accuracy of the data on densities. However by using the densities and atomic volumes of the halogens found in Table II, the molecular volumes of the cobalt halides are found to be again linear, showing that parallel relationships are maintained by the halogens free and ionic.

gens, and suggests immediately a study of other periodic group families, both metals and non-metals. In Fig. 2 the molecular volumes of the anhydrous cobalt halides are plotted as abscissas, those of the subsidiary valence compounds as ordinates. Curve a is for the 4 hexammines, and Curve b for the hexahydrates of the chloride, bromide and iodide, the corresponding fluoride hexahydrate being unknown. The curvilinear nature of both a and b is at once an experimental confirmation of the theory that although the nuclei (anhydrous halides) are in the rectilinear relationship shown in Fig. 1, and although the number of subsidiary groups
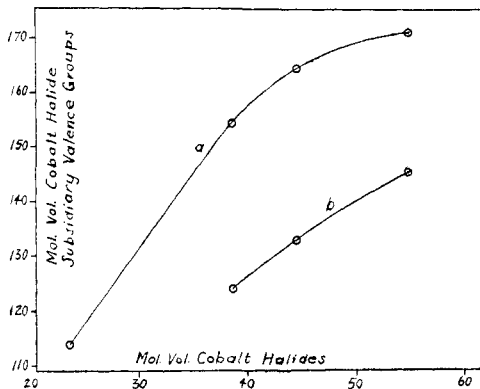

Fig. 2.

present is the same, the following effects run parallel: *the greater the difference in volume between cationic metal and anionic non-metal, the larger the cavities in the space lattice, the more stable the subsidiary valence compound and the smaller the contraction undergone by molecular groups held in the cavities.* Thus with the 4 cobalt halides the atomic volumes involved are shown in Table II.

TABLE II
ATOMIC VOLUMES OF COBALT HALIDES

Cobalt 6.77	At boiling point[24]	At T = 0[25]
Fluorine	12.14	8.85
Chlorine	22.71	16.20
Bromine	27.04	19.20
Iodine	34.42	24.33

It is obvious that the scale of stability with respect to subsidiary valence unions should increase with increase in atomic weight of the halogens. Thus cobalt iodide easily forms a nonahydrate[13] below 6.4° while cobalt fluoride cannot even form a hexahydrate. The relative stabilities of the hexammines of the iodide, bromide and chloride have been studied by Ephraim[26] by determining the dissociation temperature at a definite pressure. For an ammonia pressure of 760 mm. he found respectively 471.5, 451 and 414.5° A. The hexammine of the fluoride has not been prepared or studied prior to the work of this paper. Rough measurements have indicated however that the dissociation temperature at 760 mm. is not only lower than that of cobalt chloride but falls below 300° C. The graduation in

[24] Landolt-Börnstein, "Tables."
[25] Herz, *Z. anorg. allgem. Chem.*, **105**, 171 (1918).
[26] Ephraim, *Ber.*, **45**, 1332 (1912); *Z. physik. Chem.*, **81**, 513 (1913); **83**, 196 (1915).

stability of the hexammines from the fluoride to the iodide is therefore clearly marked. In connection with this discussion of the effects of difference in volume between cation and anion it is interesting to note what may be the effect of substituting for cobalt, metals of both smaller and greater atomic volumes. Thus if the hypothesis is correct the nickel halide hexammines should all be *more* stable than the corresponding cobalt salts, though graduated from fluoride to iodide in the same way, since the atomic volume of nickel is smaller than that of cobalt, and the manganese compounds are *less* stable. This is clearly shown by Table III adapted from Ephraim's measurements. As a matter of fact the hexammines of nickel chloride, cobalt bromide and manganese iodide have practically the same stability, so that in case of these particular cations there is exact compensation by the halogen anions.

TABLE III

EFFECT OF DIFFERENCE IN VOLUME BETWEEN CATION AND ANION ON STABILITY OF SUBSIDIARY VALENCE COMPOUNDS, SHOWN BY DECOMPOSITION TEMPERATURES

	Ni	Co	Mn
(Atomic Volume)........	6.59	6.77	7.43
Iodide Hexammine.......	508.5	471.5	448.5
Bromide Hexammine.....	482	451	405
Chloride Hexammine.....	449.5	414.5	364.5

In this case the metallic atoms are quite comparable in volume and possess the same ionic charge. With other metals whose atomic volumes are greater, or the charge greater or less than 2, it is found that the maximum number of ammonia groups which can combine varies within wide limits. In Table IV these numbers are listed as experimentally determined at the present time.

TABLE IV

MAXIMUM NUMBER OF NH_3 GROUPS COMBINING WITH METALLIC HALIDES.

20. Ce^{+++}, Au^{+++} (23?).

18. Th^{+++}.

12. Sm^{+++}, Nd^{+++}, Fe^{+++}.

9. Al^{+++}.

8. Ca^{++}, Sr^{++}

6. Be^{++}, Ni^{++}, Co^{++}, Fe^{++}, Cu^{++}, Mn^{++}, Zn^{++}, Cd^{++}, Mg^{++}, Pt^{++}, Cr^{+++}, Co^{+++}, Si^{++}, Sb^{+++}, La^{+++}, metallic Ca, Sr and Ba.

4. Li^+, Ba^{++}, Pb^{++}, Te^{++}, Sn^{++}, Sn^{++}.

3. Tl^{+++}, Ag^+, Cu^+, As^{+++}, Bi^{+++}, In^{+++}, NH_4^+, Tl^+.

2. Au^+, Sb^{+++}.

0. Na^+, K^+, Rb^+, Cs^+, Ce^{++}.

A cursory examination of this table shows at once that the numbers above 6 are generally associated with valence higher than 2, and hence large stray field, that 6 is associated with atomic volumes less than 14, and less than 6 groups with atomic volumes greater than 14, culminating in the entire absence of ammine formation with the large alkali metal

atoms. This is of course true only for cationic complexes, for with anionic complexes such as the polyhalides exactly the opposite rule is true and cesium tri-iodide, for example, is the most stable. Nickel iodide will not combine with iodine, but *tetrammine nickel iodide will* because the cation is large by virtue of the 4 ammonia groups.

From a further examination of Fig. 2 it is at once apparent that the ammonia groups in the hexammines are more compressible than the water groups in the hexahydrates as shown by the greater variation in the free space occupied by them. Table I gives the apparent volume occupied by each ammonia molecule in the hexammines: 20.10 in the iodide, 19.89 in the bromide, 19.33 in the chloride and only 15.4 in the fluoride—a remarkable larger contraction. This seems to be evidence that the effect of the fluorine atoms upon the secondary valence forces of the cobalt atom or upon each other is anomalous, although the primary valence union with the cobalt atom is entirely regular, at least from a molecular volume point of view. This is of course entirely possible and in keeping with the larger number of features of the chemistry of fluorine and its compounds which differentiate it from the other halogens. The interesting feature of cobaltous fluoride hexammine, however, lies in the fact that it is a *liquid* at the temperature at which all comparisons are made.[27] The crystal structure has been entirely broken down, and it is entirely reasonable that in the liquid an unstable ammine may exist with the ammonia groups under considerably greater compression than is usually found in space lattice cavities. It should be noted, however, that in the case of cobaltous chloride decammine discussed in the first paper of this series,[2] a still larger contraction of the ammonia groups is apparent. In all of the new compounds discussed in the present paper, calculations from the densities indicate that the average compressions of 30% over the free volume of ammonia as a liquid and 20% over the free volume of water are maintained, with the contraction inversely proportional to the difference in volume between acid group and cobalt. As indicated above, the volumes of the subsidiary groups are of course important in comparing the stabilities. It would be expected that an increase in volume of the molecular group would be accompanied by a decrease of residual valence affinity, greatest with the fluoride and least with the iodide. This might be shown by successive methylation of the ammonia. Ephraim[28] and Bonnefoi[29] have prepared many of these compounds and the results without exception verify the above statement. Thus $CoI_2.(NH_2CH_3)_6$ is less stable than $CoI_2.6NH_3$, but there is an increasingly greater effect in reducing stability in passing to the chloride, the

[27] Lithium ammines, which act similarly and are particularly interesting because of atomic simplicity, will be considered in detail in the next paper of this series.

[28] Ephraim, *Ber.*, **46**, 3742 (1913).

[29] Bonnefoi, *Ann. chim.*, [7] **23**, 353 (1881).

cavities in the space lattice of which are necessarily smaller than in the case of the iodide.

Ephraim has made the statement that metals with atomic volumes less than 14 can form hexammines. It is clear from all work on the subject however that the strength of secondary valence forces as judged by the number of groups bound and the stability, runs as a parallel phenomenon to the following properties: (1) with constant molecular group and anion to decreasing atomic volume, ionic radius, and percentage of total volume occupied by the cation; (2) with constant molecular group, anion and cation to higher valence, and hence stray field, of the cation; (3) with constant molecular group and cation to increasing atomic or radical volume, ionic radius and percentage of total volume occupied by the anion; (4) hence to increasing difference in volume between anion and cation; and (5) with constant anion and cation to decreasing volume of the ammine molecule and to increasing values of the entropy-like ratio of critical pressure to critical temperature.

Graphically, the relationships of stability, heats of dissociation and molecular volumes of ammines and hydrates are not linear to the molecular volumes of the anhydrous salts or to the atomic volumes of the halogens if halides are being considered. There is, however, one property the importance of which in a study of secondary valence has been recognized for the first time in the work of this paper. When the *percentage contraction* undergone by an anhydrous salt and a secondary valence molecular group in forming a complex is plotted against the stability of that complex represented by the absolute temperature at which the vapor pressure reaches a given value, the graph is a straight line. This remarkable parallelism between stability and percentage contraction shows that they are determined by precisely the same influences. That the one is not determined absolutely by the other is shown by the fact that anions or cations must be closely related in order to fall on the *same* straight line. The percentage contractions of the cobalt halide complexes are given in the last column of Table I. That the linearity is not a chance one has been verified by studies so far of nickel, cadmium, copper, silver and lithium ammines, all of which give the same relationship. The same is true to an even greater extent for such anionic complexes as the polyhalides of potassium, rubidium and cesium, where, because of the fact that cations and anions are members of two families of elements uniformly related to the atoms of the rare gases of the atmosphere, all of the complexes so far studied lie on the same percentage contraction curve. Thus, the compounds $KI.I_2$ and $RbBr.I_2$, which have the same stability, also have the same percentage contraction, 1.6%, which illustrates the relatively small contraction of anionic complexes. These compounds are of particular interest inasmuch as the space lattice distances for the alkaline halides are known. In the case of the two

compounds just mentioned it is clear that by starting with $RbI.I_2$ and proceeding to $KI.I_2$ and $RbBr.I_2$ of equal stability the same effect is produced by changing rubidium to potassium ion, and iodide to bromide ion. As a matter of fact the difference between the ionic radii in the two cases is exactly the same. The specific data on these compounds will be reserved for a later paper. It should be observed that the property of absolute percentage contraction is a much more rigorous one than the calculation of the apparent volume occupied by the secondary valence groups, even though interesting relative effects are possible by consideration of the latter. Thus, it has just been discovered that the ratio of the apparent volume of ammonia in lithium halide ammines to the distance in Ångstrom units between the oppositely charged ions in the anhydrous salts is constant.

Finally it may be noted that sufficient knowledge of the molecular volumes of ammonia and water has now been obtained so that it is possible to calculate with a fair approximation the molecular volumes and densities of substances particularly anhydrous which are very difficult to prepare. Cobalt nitrate may be taken as an example. An examination of the position in the stability table of the hexammine of cobalt nitrate immediately leads to assigning it a volume of about 20 to each ammonia group or 120 for all six.   Subtracting this from the molecular volume of the hexammine leaves 73.5 as the molecular volume of the anhydrous salt. Using this value and subtracting from the molecular volume of the hexahydrate leaves 81.2 or 13.5 for each water group, which is in very fair agreement with the average volume in hexahydrates.   It is only by such a method of approximation that compounds containing both ammonia and water groups may be studied.

Summary.

1. Further evidence has been presented bearing upon the theory previously outlined of the existence of "cavities" in the space lattice of solids, which may hold secondary valence groups, the sizes of the cavities depending upon the relative volumes of cation and anion and varying in a parallel fashion with the stability of secondary valence compounds.   Particular attention has been given to the preparation, properties and relationships of all the cobalt halides.   Several new compounds are reported, of chief importance among which are the hex- and tri-ammine and trihydrate of cobalt fluoride and the tetrammine of cobalt citrate.

2. Brief and preliminary consideration has been given to the methods of determining the specific gravities of unstable compounds decomposed by evacuation.

3. A new method for the ordinarily difficult preparation of monoammines is announced.

4. The constant relationship of physical properties among the halogens,

free and combined, is shown by the linearity of the molecular volumes of the cobalt halides, as well as those of numerous other metal halides, when plotted against the atomic volumes of the halogens at the boiling point. Such linearity is not maintained after the formation of ammines or hy-drates.

5. Analysis is given of 5 factors which parallel and perhaps partly determine secondary valence strength.

6. The great importance of percentage contraction in the formation of hydrates, ammines and polyhalides is shown by straight line proportion-ality to stability.

7. The theoretical approximate calculation of molecular volumes and specific gravities of compounds very difficult to prepare is briefly outlined.

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THE OXIDATION OF NITRIC OXIDE AND ITS CATALYSIS.

BY CHARLES LALOR BURDICK.

Introduction.

In a previous article[1] it has been shown that the chief reactions occurring during the absorption of the oxides of nitrogen to form nitric acid in aque-ous solution are the following

$$3NO_2 + H_2O = 2HNO_3 + NO \qquad (1)$$

$$2NO + O_2 = 2NO_2. \qquad (2)$$

Reaction 1, the reaction of nitrogen peroxide with dilute aqueous nitric acid is a very rapid reaction when carried out under conditions of efficient washing action of the gas by the liquid. It is a reaction which does not, however, proceed to completion, being halted at an equilibrium condi-tion, which in the case of nitric acid of fair concentration, is far short of complete conversion of the nitrogen peroxide. The presence of nitric oxide above a certain equilibrium concentration will prevent the reaction of absorption from proceeding at all, and only as this nitric oxide is re-oxidized and removed by the excess oxygen in the gases (according to Reaction 2) can the process of absorption go on.

Reaction 2, the re-oxidation of the nitric oxide liberated during the ab-sorption process is a slow reaction. Since the reactions of absorption and oxidation (1 and 2) progress simultaneously, and are really mutually inter-dependent, it is evident that, should it be found possible by some means to cause an acceleration in the rate of the oxidation reaction, the retarding

[1] Burdick and Freed, THIS JOURNAL, 43, 518 (1921).