was also determined by direct titration with hydrochloric acid; this method gave a value of 100.5 ± 0.9%. The yields of guanidine prepared by the above procedure were essentially quantitative and the melting point of the product was 47.5–48.5°, which is to be compared with the previously reported melting point of approximately 50°.[4]

The quartz helix balance and the procedures employed in the establishment of pressure–composition isotherms for the systems guanidine–ammonia and guanidinium chloride–ammonia (Fig. 1) are described elsewhere.[5] The phases coexistent at equilibrium are listed in Table I.

Discussion.—Earlier efforts to prepare pure guanidine have been concerned with the interaction of guanidinium salts with barium hydroxide[6,7] in aqueous solution and potassium hydroxide[8] or calcium hydroxide[4] in alcohol. All of these procedures involve the difficult dehydration of guanidinium hydroxide at low temperatures and the exclusion of carbon dioxide. Apparently only Markwald and Struwe[4] succeeded in preparing even reasonably pure guanidine. Franklin[9] has shown that guanidinium nitrate and potassium amide in liquid ammonia react to form a soluble monopotassium salt and an insoluble dipotassium salt of guanidine. The present method for the preparation of guanidine in high purity and substantially quantitative yield takes advantage of the insolubility of potassium carbonate in liquid ammonia,[10,11] the ease of elimination of water and carbon dioxide, and the ease of complete elimination of the solvent owing to its volatility.

As shown by Fig. 1, guanidine forms a 1-ammoniate which has a dissociation pressure of 220 mm. at −35.5°. This solvate is isomeric with the tetramide of carbon(IV),[9] $C(NH_2)_4$; also, this solvate may be looked upon as either guanidinium amide or ammonium guanide. In aqueous solutions guanidine is a very strong base ($pK_a = 13.65$ at 25°[12]), but Franklin[9] has pointed out that guanidine behaves as a weak acid in *liquid* ammonia solutions. In the *solid–gas reaction* observed in the present work, the guanidine molecule most likely acts as a Lewis acid to form an intermediate which could lead to either of the products suggested above.

It is of particular interest to note that guanidinium chloride is not ammonolyzed upon exposure to gaseous ammonia at −35.5°, but rather forms 2-, 3-, 4.5- and 6-ammoniates (Fig. 1, Table I). The dissociation pressures of these solvates in equilibrium with the next lower ammoniate or the deammoniated salt and ammonia gas are 60, 130, 305 and 450 mm., respectively. The 6-ammoniate of guanidium chloride is apparently analogous to the 6-ammoniate of ammonium chloride.[5] The extent to which supersaturation may occur in such systems is illustrated by Fig. 1, curve KL, which indicates metastability with respect to four invariant systems.

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Synthesis of Anhydrous Metal Halides[1]

BY GEORGE W. WATT, PHILIP S. GENTILE AND E. P. HELVENSTON

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In connection with other studies in progress in these laboratories we have devised a new method for the synthesis of anhydrous metal halides that offers considerable promise of generality of application. By this procedure, pure halides are produced in essentially quantitative yield by the interaction of the appropriate hydrated metal acetate and acetyl halide in benzene, in accordance with the general equation

$$M(C_2H_3O_2)_y\cdot zH_2O + (y + z)CH_3COX \longrightarrow MX_y + y(CH_3CO)_2O + zHC_2H_3O_2 + zHX$$

where M is a metal and X is chlorine, bromine or iodine.

Experimental.—All chemicals employed in this work were reagent grade and were not further purified.

In a typical case, 4.0 g. of finely ground hydrated metal acetate was placed in a Pyrex test-tube (18 × 200 mm.) fitted with a rubber stopper bearing a dropping funnel and a filter stick. Following addition of 15 ml. of benzene, the mixture was slurried with a magnetic stirrer and treated slowly with a 10% excess of the appropriate acetyl halide. The reaction mixture was stirred for 30 min., the precipitated metal halide was allowed to settle, and the mother liquor was drawn off through the filter stick. The residue was retreated with benzene and acetyl halide to ensure complete conversion, after which the supernatant liquid was removed by filtration and the solid product was washed three or four times with 20-ml. portions of dry benzene. The product contained in the reaction vessel in an atmosphere of dry oil-pumped nitrogen was transferred to an oven and dried for 3 hr. at 200° in a nitrogen atmosphere and thereafter transferred to a dry-box for sampling and analysis. The results obtained with ten different halides are given in Table I.

TABLE I

ANALYTICAL DATA

	Anal. for halide[b]			
	Chloride		Bromide	
Halide[a]	Found	Calcd.	Found	Calcd.
CuX_2	51.6	52.8	71.2[e]	71.7
CdX_2	38.4	38.7	58.6	58.8
MnX_2[c]	56.0	56.4	73.7	74.4
CoX_2	54.2	54.6	72.7	73.0
NiX_2[d]	54.0	54.8	72.9	73.1

[a] The starting materials were the 1-hydrate of the acetate of copper(II), the 2-hydrate of the acetate of cadmium(II), and the 4-hydrates of the acetates of manganese(II), cobalt(II) and nickel(II). [b] Determined by the Volhard method. [c] Slow reaction; acetyl chloride added first; mixture boiled for 5 min. after second addition of acetyl chloride. [d] Same as footnote *c* except that reaction mixture was finally stirred for 12 hr. at room temperature. [e] Bromide decomposes slowly at 200°; hence, drying for 2 hr. at 150° was used.

In a similar experiment, bismuth(III) chloride was converted quantitatively to the corresponding iodide by treatment with acetyl iodide. *Anal.* Calcd. for BiI_3: Bi, 35.4. Found[2]: Bi, 34.9.

Discussion.—Although complete data on yields and purity are not available, similar use of the acetates of aluminum(III), chromium(III), thallium(I), neodymium(III) and samarium(III) indicates that the reactions lead to the corresponding an-

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[1] This work was supported in part by the U. S. Atomic Energy Commission, Contract AT-(40-1-)-1639.

[2] N. C. Blasdale and W. C. Parle, *Ind. Eng. Chem., Anal. Ed.*, **8**, 352 (1936).

hydrous halides. Encouraging results have also been obtained through the use of hydrated salts other than acetates, *e.g.*, copper(II) sulfate 5-hydrate and thorium(IV) nitrate 4-hydrate. The exact procedural details for any given case are subject to minor variations depending upon the solubility of the product and the reactivity of the salt employed as the starting material as well as that of the acetyl halide. Acetyl iodide is relatively unstable and should be prepared as needed.[3] Highly covalent halides, such as chromium(III) bromide, that are soluble in benzene may be prepared by this method by boiling off the excess acetyl halide, benzene, and the other reaction products. Alternatively, other organic liquids in which the product halides are less soluble may also be used as the reaction media.

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Studies in Low Concentration Chemistry. X. Further Observations on Yttrium

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Yttrium at concentrations below 10^{-5} *M* in aqueous solution has been the subject of several previous investigations.[1] This paper is a continuation of studies into the radiocolloidal properties of this element and also presents some adsorption and solvent extraction data.

Experimental

Materials.—Strontium-90 in equilibrium with its radioactive daughter yttrium-90 was obtained as the chloride from Oak Ridge National Laboratory. Carrier-free yttrium-90, a β-emitter with a half-life of 65 hr., was separated from the parent element by a slight modification of the method of Schweitzer, Stein and Jackson.[1]

A labeled 10^{-2} *M* yttrium chloride solution was prepared by dissolving yttrium oxide in concentrated hydrochloric acid, adding yttrium-90, and diluting with distilled water. Labeled 10^{-4}, 10^{-5}, and 10^{-8} *M* solutions were prepared by appropriate addition of tracer and dilution of the 10^{-2} *M* stock solution. Norit A Decolorizing Carbon (Pfanstiehl Chemical Co.) was used as an adsorbent. All other chemicals were of C.P. reagent grade quality.

Apparatus.—Centrifugations were carried out in 0.7-ml. Pyrex glass tubes which were rotated in a Misco Microcentrifuge at about 25,000 times gravity. The solvent extractions were performed in a 25-ml. round bottom flask, the contents of which were stirred by a mechanical stirring motor attached to a glass stirrer which rotated in a sleeve of rubber tubing. The rubber tubing was placed in a one-hole rubber stopper which sealed the flask. The liquids in the extraction vessel were maintained at 25.0 ± 1.0° by keeping the vessel partially immersed in a constant temperature bath. Twelve-ml. weighing bottles were employed as sample containers for the adsorption experiments. These bottles were shaken in a Dubnoff Shaking Apparatus at room temperature. All *p*H values were measured by a Beckman Model G-2 Glass *p*H Meter equipped with microelectrodes.

Radioactivity Measurements.—All solutions were sampled by taking 0.100 ml. of liquid with a 0.100-ml. micropipet, placing the liquid on a copper planchet, and then evaporating to dryness under a heat lamp. The activities of the samples were determined with a Nuclear D-34 end-window Geiger tube mounted in a Tracerlab 64-Scaler. All activities were counted for a sufficiently long time to give a maximum standard deviation of 1%.

Centrifugation Experiments.—Ten-ml. portions of the radioactive 10^{-8} *M* yttrium chloride originally 0.1 *N* in hydrochloric acid were adjusted to various *p*H values using hydrochloric acid or sodium hydroxide solution. Three samples at each *p*H value were then placed in separate centrifuge tubes and allowed to stand for 1 hour so that adsorption onto the glass could come to equilibrium. The solutions were sampled and, after centrifugation for 30 minutes, they were resampled and the *p*H values were redetermined. The differences in radioactivities were used to calculate the percentages of yttrium removed. A similar procedure was followed with the labeled 10^{-5} and 10^{-2} *M* solutions.

Solvent Extractions.—Ten-ml. portions of the carrier-free yttrium solution originally 0.1 *N* in hydrochloric acid were adjusted to various *p*H values with hydrochloric acid or sodium hydroxide solution. Three ten-ml. portions at each *p*H value were sampled, placed in the extraction apparatus, and then 12 ml. of acetylacetone was added. The use of these volumes of the two phases gave equal final volumes due to evaporation and mutal solubility. After stirring each sample for 1 hour, the two liquid phases were separated, each phase was sampled, and the *p*H value of the water phase was redetermined. From the radioactivities, the percentage yttrium removed from the water phase was calculated. Similar experiments were performed using the labeled 10^{-8}, 10^{-5} and 10^{-2} *M* yttrium solutions.

Adsorption Experiments.—Five-ml. portions of the carrier-free yttrium solution originally 0.1 *N* in hydrochloric acid were adjusted to various *p*H values using hydrochloric acid or sodium hydroxide solution. Three five-ml. portions at each *p*H value were placed in weighing bottles, allowed to stand for 1 hr. to reach adsorption equilibrium, sampled, and then the desired amounts of carbon were added. After shaking for 1 hr., the carbon was allowed to settle, and each portion was resampled. From the radioactivities of the samples, the percentages of yttrium adsorbed onto the carbon could be calculated. A similar procedure was followed using the labeled 10^{-8}, 10^{-5}, 10^{-4} and 10^{-2} *M* yttrium solutions.

Results and Discussion

The results of the centrifugation experiments are presented in Fig. 1, all *p*H values being final ones. These data verify the previous observation that yttrium in very low concentrations forms aggregates under certain solution conditions.[1] It also has been confirmed that as the concentration of yttrium increases, the concentration of hydroxide ion associated with the production of centrifugable

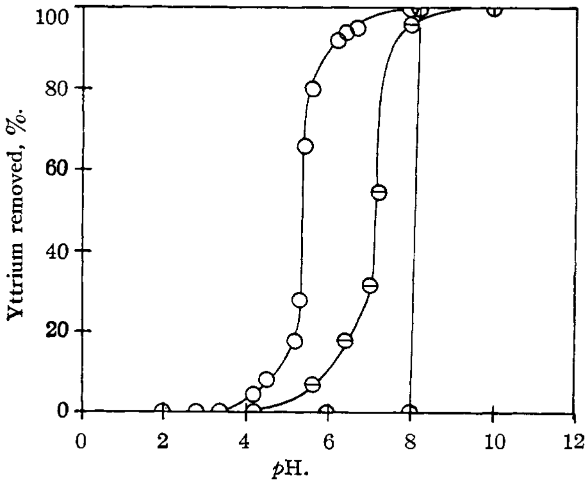

Fig. 1.—Per cent. yttrium removed by centrifugation *versus* *p*H at yttrium concentrations of: 10^{-8} *M*(○); 10^{-5} *M*(⊖); 10^{-2} *M*(ϕ).

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[1] J. D. Kurbatov and M. H. Kurbatov, *J. Phys. Chem.*, **46**, 441 (1942); G. K. Schweitzer, B. R. Stein and W. M. Jackson, THIS JOURNAL, **75**, 793 (1953); G. K. Schweitzer and W. M. Jackson, *ibid.*, **76**, 3348 (1954).