

that the amorphous colloidal manganese dioxide obtained by reducing permanganate with acetone in the presence of variable amounts of alkali undergoes changes comparable with those of the emulsoid-suspensoid type of manganese dioxide. On the basis of certain results of other workers the attempt was made to interpret the experimental data for both types of colloids on the basis of two types of dynamic equilibria: (1) molecular association \rightleftharpoons molecular dissociation; (2) hydration \rightleftharpoons dehydration. It was found that the experimental observations readily fit into such an interpretation.

It is thought that the point of view developed here will be of much interest in the elucidation of a number of other chemical and biological phenomena and further work along these lines is under way.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF COLORADO.]

NONAQUEOUS SOLUTIONS.

I. CHEMICAL REACTIONS IN ISOAMYL ALCOHOL SOLUTIONS.

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Not many investigations have been made of reactions between inorganic salts in solvents other than water. The most extensive study in this field is that of A. Naumann¹ and his students, who have determined the solubilities of a number of salts and their reactions in acetone, ethyl acetate, methyl acetate, pyridine and acetonitrile. Aside from these investigations, there may be gleaned from chemical literature a considerable number of isolated observations in this field.

The solubility of anhydrous inorganic salts in organic solvents has received considerable attention, but there is much uncertainty as to the dependability of some of the earlier measurements. Values obtained by different investigators are often widely different, and there have been found some cases in which the effect of temperature on solubility is wrongly stated.

The following paper records observations of reactions between anhydrous inorganic salts dissolved in dry isoamyl alcohol. Such salts were used as dissolve readily in the solvent.

Experimental Details.

All glassware used in this work was first carefully cleaned and dried in the usual way. Just previous to use each piece was further dried by passing dry air through it for at least half an hour, the air for this purpose being dried with sulfuric acid and phosphorus pentoxide.

¹ *Ber.*, 37, 3600, 4328, 4609 (1904); 42, 3789 (1909); 43, 313 (1910); 47, 247, 1369 (1914).

The isoamyl alcohol was allowed to stand over anhydrous copper sulfate for several days, the mixture being frequently shaken. The alcohol was then distilled in a dry still and the middle portion saved for use. During the distillation and always thereafter the alcohol was protected from the air by means of tubes containing anhydrous copper sulfate.

The salts used were air-dried for many hours at temperatures which other investigators have found suitable. In the case of copper chloride the salt was dried at 160° in a stream of dry hydrogen chloride. The ferric chloride used was prepared by passing dry chlorine over hot iron filings. After being dried the salts were kept in desiccators over sulfuric acid or phosphorus pentoxide until used.

The solutions were made up as follows: Some of the dried salt was placed in a flask and the isoamyl alcohol at once syphoned in. The flask was then stoppered with a stopper carrying a tube filled with dry copper sulfate and allowed to stand a few days. The saturated solution was then poured quickly into a larger flask and enough of the solvent syphoned in to make an approximately half saturated solution. The solutions were at all times kept protected from the air until used.

The hydrogen sulfide used was dried by passing first through towers filled with granular calcium chloride and finally through towers filled with glass wool and phosphorus pentoxide. The hydrogen chloride was dried by passing several times through concentrated sulfuric acid. The ammonia was passed through towers filled with quicklime and then through towers packed with glass wool and phosphorus pentoxide.

Results.

Cobalt Chloride Solution.—(a) Cobalt chloride dissolves readily in isoamyl alcohol to form a deep blue solution. It is to be noted that aqueous solutions of cobalt chloride are pink; methyl alcohol solutions are blue when very concentrated but become pinkish blue and finally pink when diluted with the alcohol; ethyl alcohol solutions of the salt are blue at all dilutions and the same is true of the isoamyl solutions. Addition of hydrogen chloride to either the aqueous or the methyl alcohol solution of cobalt chloride gives a pure blue solution.

(b) Hydrogen sulfide partially precipitates the cobalt as a black cobalt sulfide. This settles readily, leaving a blue supernatant liquid.

(c) Ammonia produces a pale rose-red precipitate containing cobalt, ammonia and chlorine. After drying in the air, the compound has the following composition:

31.2% Co, 41.2% Cl, 27.4% NH_3 . Gram atoms 1:2.1:3.04

The compound therefore has the formula $\text{CoCl}_2 \cdot 3\text{NH}_3$.

Biltz and Fetkenheuer¹ have shown that the compounds $\text{CoCl}_2 \cdot 6\text{NH}_3$ and $\text{CoCl}_2 \cdot 2\text{NH}_3$ form mixed crystals having approximately the for-

¹ *Z. anorg. Chem.*, 89, 97 (1914).

mula $\text{CoCl}_2 \cdot 3\text{NH}_3$, but that there is no true compound of this formula.

Mercuric Iodide Solution.—(a) Mercuric iodide is slightly soluble in cold isoamyl alcohol, but dissolves readily in the hot alcohol. The solubility curve has been determined by Laszczyński.¹ On cooling a hot saturated solution, the mercuric iodide separates out in yellow crystals. These go slowly over to the red modification on standing at room temperature.

(b) Hydrogen sulfide throws out an orange-yellow precipitate. If the stream of hydrogen sulfide be passed through the solution for a long time, the precipitate becomes brown and finally black. The solution meanwhile acquires the exceedingly disagreeable odor of amyl mercaptan (the odor of the skunk is due chiefly to butyl mercaptan, and the amyl mercaptan is no less offensive). If the solution be saturated with hydrogen chloride before the hydrogen sulfide is passed in, no precipitation occurs.

(c) Ammonia has no effect on the cold isoamyl alcohol solution, which contains but little dissolved iodide, but if ammonia be passed into the hot concentrated solution, a lemon-yellow compound is obtained.

Mercuric Chloride Solution.—(a) Mercuric chloride dissolves in isoamyl alcohol to form a colorless solution. On cooling a saturated solution, the salt separates out in white crystals.

(b) Hydrogen sulfide produces a yellow precipitate which becomes brown and finally black if the stream of hydrogen sulfide be long continued. The solution acquires the odor of amyl mercaptan as in the case of the mercuric iodide solution. The catalytic effect in forming the mercaptan is apparently not limited to the iodide.

(c) Ammonia produces a white precipitate containing mercury, chlorine and ammonia in the gram atom ratio of approximately 2-6-3. Closely checking results could not be obtained on analyzing different samples of the compound. If the compound analyzed were pure, it is not evident what its structure may be.

(d) Selenium dioxide solution precipitates a small amount of a white compound.

Copper Chloride Solution.—(a) Copper chloride dissolves in isoamyl alcohol to form a dark green solution. Warming the solution changes the color to a brownish green, the solution becoming almost opaque.

(b) Hydrogen sulfide precipitates black copper sulfide, the reaction being quantitative.

(c) Addition of calcium bromide solution causes the copper chloride solution to become deep brown in color. Copper bromide dissolves in isoamyl alcohol to form a solution which has the same deep brown color.

¹ *Ber.*, 27, 2285 (1894).

(d) Cadmium iodide solution precipitates cuprous iodide and liberates iodine, the reaction being the same as occurs in aqueous solutions.

(e) Ammonia precipitates at first a green compound, but this changes to a blue compound if the ammonia stream be continued for a few minutes. The blue compound is not stable in the air but liberates ammonia and goes over into the green compound. This green compound, dried in the air, gives the following analysis:

37.62% Cu, 41.64% Cl, 20.74% NH₃. Gram atoms 1:1.986:2.062

The formula is, therefore, CuCl₂.2NH₃.

(f) Hydrogen chloride changes the color of the solution from a deep green to a yellowish brown.

Cobalt Nitrate Solution.—(a) Cobalt nitrate is moderately soluble in isoamyl alcohol, giving a wine-red solution. This color is in striking contrast to the blue of the cobalt chloride solution.

(b) Hydrogen chloride at once changes the color of the solution to a blue.

(c) Hydrogen sulfide precipitates the cobalt as the black sulfide, the reaction being almost complete. This contrasts with the very incomplete precipitation obtained in cobalt chloride solution.

(d) Ammonia produces a dirty green precipitate which settles readily, leaving a colorless supernatant liquid.

(e) Calcium bromide solution changes the color of the solution to a deep blue, indicating the formation of the bromide of cobalt.

Zinc Chloride Solution.—(a) Ammonia causes a white precipitate. This, dried in the air, has the following composition:

37.82% Zn, 41.39% Cl, 20.85% NH₃. Gram atoms 1:2.03:2.1

The compound therefore has the formula ZnCl₂.2NH₃.

Cadmium Iodide Solution.—(a) Hydrogen chloride causes the solution to become deep brown in color due to the liberation of iodine.

(b) Selenium dioxide solution produces a rusty red precipitate.

(c) Ammonia produces a very heavy white precipitate. Dried in the air, this has the following composition:

27.19% Cd, 64.39% I, 8.37% NH₃. Gram atoms 1:2.09:2.03

The compound has the formula, CdI₂.2NH₃.

(d) Hydrogen sulfide precipitates a compound having the yellow color of cadmium sulfide, but which is a double salt containing iodine, probably CdI₂.2CdS. The precipitate is at first extremely finely divided, passing completely through filter paper. After passing in hydrogen sulfide for several hours the precipitate coagulates so that a little of it is retained on filter paper. The solution smells faintly of mercaptan.

Ferric Chloride Solution.—(a) Ferric chloride dissolves in isoamyl alcohol to form an amber-colored solution. On standing, a rust-colored precipitate slowly forms in the solution.

(b) Ammonia precipitates a reddish brown compound resembling ferric hydroxide.

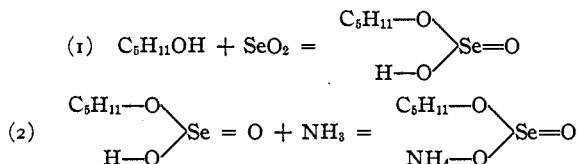
(c) Hydrogen sulfide at first precipitates a dark brown compound. On continuing the stream of hydrogen sulfide the color of the precipitate changes to straw yellow.

(d) Selenium dioxide solution causes the ferric chloride solution to assume a somewhat lighter color. On standing, red selenium separates.

Selenium Dioxide Solution.—(a) Selenium dioxide dissolves readily in isoamyl alcohol, giving a solution which reacts acid to litmus. On standing for several days, red selenium slowly separates out.

(b) Hydrogen sulfide produces a dark orange-colored precipitate.

(c) Ammonia throws out a white compound. On standing in the air, this slowly decomposes, liberating red selenium. Light hastens the decomposition somewhat. The compound is soluble in water, from which solution acid stannous chloride throws out red selenium. Washed with clean ether and dried in the air for an hour, the compound contains about 8% of free ammonia (titrated directly with standard hydrochloric acid in water solution) and 16% total ammonia (distilled off with potassium hydroxide, caught in standard hydrochloric acid and the excess of standard acid titrated with standard ammonia solution). On standing over sulfuric acid, the free ammonia content rapidly decreases and in two days amounts to only a fraction of a per cent. The combined ammonia remains constant at about 8%. It appears probable that the free ammonia is mechanically held in the precipitate by a little of the mother liquor. On heating the dry compound, ammonia, amyl alcohol and selenium dioxide are obtained. This would indicate that the compound is amyl ammonium selenite, $(\text{NH}_4\text{C}_5\text{H}_{11})\text{SeO}_3$, which contains 7.86% of ammonia. The reactions involved would be represented as follows:



Ammonium Thiocyanate Solutions.—(a) Hydrogen chloride precipitates a white compound which proved to be ammonium chloride.

(b) Copper chloride solution causes a dark brown precipitate.

(c) Ferric chloride solution gives a blood red coloration as in aqueous solution.

(d) Nickel nitrate solution precipitates ammonium nitrate.

Behavior of Methyl Orange in Isoamyl Alcohol Solution.—Methyl orange dissolves sparingly in isoamyl alcohol to form a yellow solution. If ten cc. of this solution be shaken with an equal volume of 0.5 *N* hydro-

chloric acid in water solution, both the water layer and the alcohol layer become pink. If, however, the concentration of the acid used be 0.125 *N*, the water layer will become pink but the alcohol layer will remain yellow. The mid-point between the pink and the yellow color in the alcohol layer is obtained when the acid used has a concentration of about 0.2 *N*. If nitric acid be used instead of hydrochloric, the mid-point is obtained with nearly the same concentration of acid as in the case of the hydrochloric. With sulfuric acid solutions, however, the yellow color persists in the alcohol layer until nearly normal acid is used.

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STANDARD CELLS AND THE NERNST HEAT THEOREM.

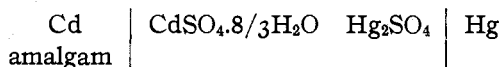
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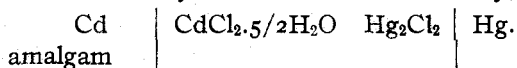
A considerable amount of exact information has been accumulated as to the reactions, the electromotive forces and the temperature coefficients of the various combinations of standard cells. For the purposes of thermodynamic calculation over the ordinary range of temperature these data are sufficient. On the other hand, if it be desired to extend the calculations over a wide range of temperature it is necessary in addition to know the specific heats of the several reacting substances. With this information secured standard cells provide a most interesting means of testing the Nernst heat theorem.

The assumptions made by Nernst are applicable only to condensed systems, so that in case the system consists in part of a solution, calculations according to the theorem of Nernst can only be made below the cryohydrate temperature. At temperatures above this the Gibbs-Helmholz equation must be used. Consequently, with standard cells, it is necessary to carry out the thermodynamic calculations in two stages, below the cryohydrate temperature with the aid of the Nernst heat theorem, above this temperature with the fundamental equation.

The present work was undertaken in order to test the applicability of the Nernst heat theorem to the well-known Weston standard cell



and to a standard cell lately studied in this laboratory,¹



The electromotive forces and the temperature coefficients of these cells

¹ Lipscomb and Hulett, *THIS JOURNAL*, 38, 20 (1916).