ART. LVI.—*Notes on Silver*; by M. CAREY LEA.

Action of Ammonia.—Aqueous ammonia is supposed to be without action on normal silver but this is not so: under favorable conditions, silver is gradually taken up by this solvent.

The first experiments were made with silver reduced from the nitrate by the action of sodium hydroxide and milk sugar. The silver was very carefully purified from any possible trace of oxide. Placed in contact with ammonia for a few hours, silver was taken up. Its presence could be recognized either by ammonium sulphide or by adding a drop or two of hydrochloric acid and then supersaturating with dilute sulphuric acid; a dense cloud of silver chloride forms and this result can be obtained any number of times in succession by acting with ammonia on the same portion of silver.

A similar reaction was obtained with silver reduced from chloride by cadmium and hydrochloric acid removing afterwards all traces of cadmium. Silver reduced in this way is liable to contain traces of chloride. These were removed by covering the silver with strong ammonia, letting it stand over night and thoroughly washing out. This was repeated five times. From this silver, ammonia by twenty-four hours contact always took up enough to give a dense white cloud when treated as above.

Portions of solutions obtained in the last mentioned manner were evaporated to dryness over the water bath and left brownish black films. These were non-explosive and therefore did not consist of silveramine: they yielded a large proportion of silver to acetic acid, leaving behind a little metallic silver. The ammonia therefore, does not dissolve the silver as metal but as oxide. The presence of a little metallic silver in the residue left by evaporation was probably due to slight traces of oxidable organic matter contained in the ammonia. This opinion was confirmed by the fact that the solution when heated acquired a transparent red color.

It appears therefore that in the presence of ammonia, silver has a tendency to oxidize, for when the silver was placed in a vial with an air-tight fitting stopper, filling it about half full, and was then completely filled with liquid ammonia and tightly closed, it was found that in twenty-four hours a mere trace of silver was taken up. On the other hand when the silver was placed in a flat basin and merely moistened with ammonia more silver was taken up in five minutes than in the preceding case in twenty four hours.

This action of ammonia in promoting oxidation recalls its behavior with cobaltous salts and with copper. It is probably

the only case in which silver is oxidized (at ordinary temperatures) by atmospheric oxygen.

Action of Dilute Sulphuric Acid.—It is generally held that silver is insoluble in cold dilute sulphuric acid. Almost any form of silver, providing it is finely divided, is slightly soluble in sulphuric acid diluted with four or five times its bulk of water. With more dilute acid different varieties of silver act very differently. The most easily attacked is that which is obtained by reducing the oxide with alkaline hydroxide and milk sugar; from this a distinct trace is dissolved by sulphuric acid diluted with 100 times its bulk of water. From silver reduced from the chloride by cadmium this very dilute acid takes up nothing.

Nitric acid, sp. gr. 1.40, diluted to ten volumes and allowed to stand for an hour with finely divided silver, took up an extremely faint trace.

Hydrochloric acid, sp. gr. 1.20, was totally without action. The silver after being well boiled with water to remove every trace of acid, dissolves completely in nitric acid.

Acetic acid has no action upon metallic silver.

Various Reactions of Normal Silver.

Normal metallic silver even in a state of very fine division does not abstract the slightest trace of nitric acid from perfectly neutral cupric nitrate obtained by acting on pure cupric sulphate with barium nitrate. After fifteen hours of contact not a trace of silver had been dissolved.

But silver easily reduces cupric chloride with formation of purple photochloride. If the copper salt is present in slight excess the silver is so thoroughly acted upon that nitric acid does not extract a trace of it from the purple photochloride.

Metallic mercury instantly reduces silver nitrate but metallic silver takes chlorine from corrosive sublimate. The precipitate contains calomel and blackens with ammonia.

Silver in fine division slowly reduces a neutral solution of potassium permanganate.

Silver nitrate, as is well known, is reduced by ferrous sulphate, or ammonia ferrous sulphate, the iron at the same time becoming peroxidized and the silver assuming the gray metallic form. On the other hand silver powder rapidly reduces a neutral solution of ferric sulphate. A solution of iron alum readily dissolves metallic silver without the aid of heat;* in a few seconds the solution strikes a blue color with potassium

* The statement in the new *Encyclopédie Chimique* that heat is required and that the metal separates again on cooling (Tome iii, cahier 15, p. 248) appears to be incorrect.

ferricyanide and if the iron alum is in excess the whole of the silver is dissolved. It has been before noticed that the reactions between silver salts on the one hand and iron salts on the other are to some extent reversible, the observations just described place the matter in a somewhat clearer light. With a view of ascertaining whether ferrous sulphate could be completely oxidized by argentic oxide a portion of the ferrous solution was treated with successive portions of the oxide until the latter was no longer affected by it. But when this stage was reached the solution no longer contained a trace of iron, the whole of it had entered into combination with the silver. This combination is perfectly black and may probably have consisted of the compound described by H. Rose, as Ag_2O , 2FeO Fe_2O_3 and obtained in the same way.

When ammonia iron alum is placed in contact with finely divided silver in considerable excess in a tightly closed vial the solution after a few days standing with frequent shaking acquires a deep red color. This may last for a week or more. The solution then decolorizes and becomes greenish but still contains abundance of ferric salt. Thus it appears that although silver has a powerful reducing action on ferric salts the action is self-limited and ceases long before complete reduction is effected for after many weeks contact in a closed vial there are abundant indications of the presence of ferric salt, although silver has been present in large excess.