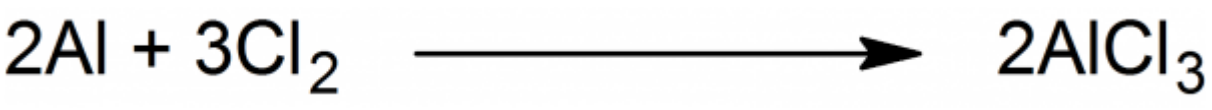
Preparation of aluminum chloride



Manganese dioxide (pyrolusite), potassium permanganate, potassium dichromate or any other oxidizing agent, suitable for generating chlorine from hydrochloric acid, is placed 1000 ml round-bottom flask **A**. Through the two-hole stopper a dropping funnel is attached and a glass delivery tube is connected with the first of the two wash bottles, as shown **B**, **B.** The first bottle contains water for absorption any hydrochloric acid gas which may pass together with generated chlorine, and concentrated sulfuric acid in the second, in order to dry the chlorine thoroughly. A hard glass tubing **C** about 85 cm long and 1 cm ID is connected to the second wash bottle with a piece of delivery tube and a stopper, as shown in the figure. The other end of the glass tube is connected to the receiver **D,** which serves for escaping fumes of chlorine.

Into the reactor tube **C** 5 g of aluminum chips or turnings are placed, which have been washed with ether or petroleum ether to remove oil, and then thoroughly dried. Aluminum is placed near the end of the tube where the chlorine enters, the larger part of the tube being kept clear. When all the apparatus is tightly joined together, chlorine gas is generated by adding 40 % of hydrochloric acid into the flask **A**. The flask is gently warmed until a vigorous but steady evolution of chlorine gas is established. In the beginning of the experiment, the chlorine passes through the apparatus until all the air is expelled. Then the reactor tube **C** containing the aluminum is heated with the gas burner. The content becomes red-hot and then begins to glow and scintillate as the reaction takes place. The aluminum chloride sublimes over into the cool end of the tube, where it condenses as a pale yellow sublimate. The heating is continued as long as the residue glows and when on prolonged heating it becomes black, the burner is removed and the tube is allowed to cool, while the stream of chlorine continues to pass through the apparatus. the reactor tube **C** is disconnect while still warm, and obtained aluminum chloride is collected, being careful not to mix any of residue with it. The aluminum chloride should be transferred at once into a perfectly dry bottle, which has been previously weighed with its stopper. All moisture must be avoided, and the transfer from the tube to the bottle must be made as quickly as possible after disconnecting the tube. The reactor tube **C** may be recharged at once with another 5 g of aluminum and the process repeated. The final yield of anhydrous aluminum chloride from 10 g of metallic aluminum is around 35-38 g.

For the preparation of larger quantities of the anhydrous aluminum chloride, sufficiently pure for synthesis purposes used in Friedel–Crafts reaction, 1600 ml of 40% concentrated hydrochloric acid is placed into a 3000 ml round-bottom flask **A**. A dropping funnel is attached so that concentrated sulfuric acid (d=1.84) may be dropped into the hydrochloric acid without running down the sides of the flask. The glass delivery tube is connected closely with the two gas wash bottles **B**, **B**, each containing concentrated sulfuric acid (d=1.84). A long glass tube (reactor) with large diameter (18 mm) is attached and connected through the stopper with the bottle **D**, by allowing the end to extend only 2 to 3 mm into the bottle. Through this same stopper an outlet tube **E**, having a diameter of 1 cm, is attached. To prevent clogging of the outlet tube **E** glass rod or a brass or copper wire may be passed through it to push back into the bottle any deposit of aluminum chloride. A loose plug of asbestos is placed into the reactor tube at the base of the drawn-out end, and then aluminum turnings (previously treated ether or petroleum ether in order to remove oil) till the tube is almost full. Another loose asbestos plug is placed in the front of the glass tube.

When all-glass apparatus is tight and ready to perform experiment, concentrated sulfuric acid (d=1.84) is placed into the separatory funnel, and added drop-wise into the concentrated hydrochloric acid in the flask **A**. After introducing about 75 to 100 ml of sulfuric acid, the temperature of the flask begins to rise, and soon a copious evolution of hydrochloric acid gas begins, which can easily be controlled by regulating the dropping of the sulfuric acid. The strong stream of hydrogen chloride gas is passed through the apparatus for from 10 to 15 minutes until all the air is expelled. In the beginning, the long glass tube is heated slowly, by burning a low flame on all the burners. Gradually the temperature should be raised of the first burner in line to a low red heat at the inlet end, and keep it so until the metal has nearly all been converted into aluminum chloride and sublimed away. The burners is turned on by twos and threes as the metal slowly burns away until all of it has been converted to aluminum chloride and passed over into the bottle. During the experiment, the long glass tube should not be over heated because it can cause fusion of aluminum into globules, and the action of

the hydrogen chloride gas becomes exceedingly slow and tedious. The stream of hydrogen chloride gas must be fairly rapid, and the outlet tube must not be allowed to become clogged with a deposit of aluminum chloride. It is generally necessary to heat the tube between the furnace and the bottle **D** with a Bunsen burner. The stopper may be protected from burning by an asbestos plate. As soon as the experiment is finished, the bottle **D** containing the aluminum chloride is scraped while still warm and transferred in a desiccator over concentrated sulfuric acid. The advantages of this process are the easy control of the gas stream and the usually better yield than from. Usually from 190 to 200 g of aluminum chloride may be obtained from 50 g of aluminum.

A solution of aluminum chloride can be prepared directly by the action of hydrochloric acid on the aluminum, but if this solution is evaporated to dryness, the solid that is left is the aluminum oxide instead of the aluminum chloride. Hydrolysis is prevented by hydrochloric acid, and the aluminum chloride hexahydrate can be crystallized from an hydrochloric acid solution. The solution of aluminum chloride is saturated with hydrogen chloride, which not only drives back hydrolysis but also reduces the solubility of the aluminum chloride hexahydrate.

13.5 g of aluminum turnings are placed in a 500 ml flask containing 50 ml of water. To this flask, 125 ml of concentrated hydrochloric acid are added dropwise until a vigorous reaction has started and finally as rapidly as may be without producing too violent a reaction. The 125 ml of concentrated hydrochloric acid should just suffice to dissolve the aluminum turnings. Unless it is perfectly clear, the solution is filtered, the filtrate is returned to the 500 ml flask. To prevent hydrolysis of aluminum chloride the hydrogen chloride gas is pass into the flask containing the aluminum chloride solution. The end of the delivery for gaseous hydrogen chloride tube dipping into the solution must be at least 1.5 cm in diameter, else it will become stopped with the precipitated aluminum chloride hexahydrate. The flask containing aluminum chloride hexahydrate solution is further fitted with an exit tube which will lead any excess of hydrogen chloride gas to within few centimeters of the surface of water in a bottle. The flask with the solution of aluminum chloride is immersed in the ice-water bath, and hydrogen chloride gas is passed into the solution until it is saturated. The crystalline precipitate of aluminum chloride hexahydrate are collected in a funnel and dried as completely as possible with suction while pressing the crystal mass with a glass stopper. The aluminum chloride hexahydrate is additionally dried in the desiccator over solid sodium hydroxide for several days to completely remove the excess of hydrochloric acid.

Synthetic inorganic chemistry, by A. A. Blanchard, 212-213, 1936