AMERICAN CHEMICAL INDUSTRIES

The Dow Chemical Company

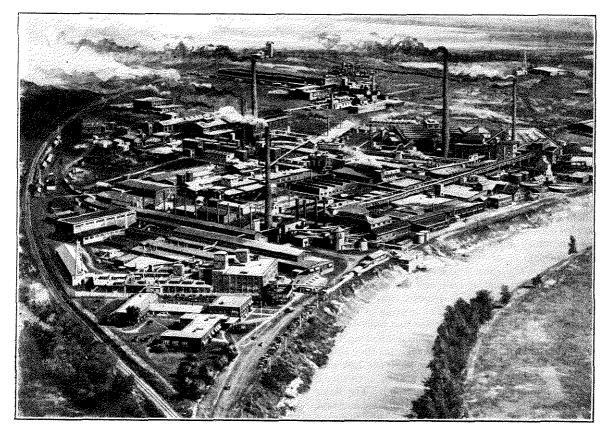
HE early history of The Dow Chemical Company is merged in the history and expansion of several smaller companies, notable of which was the Midland Chemical Company, first organized as a partnership in 1890 and later as a corporation in 1892. The Dow "blowing-out" process for bromine (Patent Application, 1889) was the basis for operation in all instances. Though ferric bromide constituted the first salable commodity, it was not long before use was made of cheap potash fiquors from lixiviation of wood ashes of neighboring sawmills, and by 1892 pure potassium bromide crystals were offered on the market.

The electrical liberation of bromine from raw brine is the first recorded instance of successful application of electrolysis in commercial production of nonmetallic elements. The need of a generator of sufficient capacity to furnish the required current caused no end of discomfiture. After persistent efforts on the part of the general manager, Herbert H. Dow, there was finally secured a generator of 2000 amperes at 15 volts. A plant was erected in 1890 for the liberation of bromine from brine by bringing this brine into contact with a multiplicity of units in each electric cell of a four-cell series. So successful was the Dow electrolytic process for liberation of bromine that its adaptation for chlorine was soon under way. A small isolated plant for the manufacture of bleaching powder was operated under the name of the Dow Process Company in 1895. On May 15,

1897, The Dow Chemical Company was incorporated under the laws of the State of Michigan to take over and enlarge this bleaching powder plant to an output of 9 tons of bleach per day. In 1900 the capacity of this bleaching powder plant was doubled. In this same year The Dow Chemical Company took over the bromine producers, the Midland Chemical Company, whose bromine-free brine had become the raw material for chlorine on the part of the new company. In each of the succeeding years, 1901 and 1902, the capacity of the bleaching powder plant was doubled, until the output actually reached 70 tons per day.

The Dow electrolytic cell of crude beginnings had slowly developed into a practical and efficient unit, well adapted for the production of chlorine. But with increased capacity it became necessary to discover larger fields for the utilization of chlorine. The manufacture of carbon tetrachloride from carbon bisulfide and sulfur chloride and its subsequent reduction to chloroform was thus begun; up to the present, strange as it may seem, no better process for the latter has come to the attention of chemists.

The next organic chemical venture was the inauguration of an oxidation process for benzoic acid—that is, the action of bleaching powder upon benzyl chloride. German competition, however, soon forced the price of benzoic acid to eighteen cents a pound and this curtailed somewhat the activity of this particular organic venture.



Airphoto of The Dow Chemical Company, Midland, Mich.

In the years just preceding the war bromides of every description were being manufactured at Midland. The progress toward isolation of calcium and magnesium chloride from the raw brine was then in its early stages and by the close of 1914 there followed large sales of magnesium chloride for use in stucco.

During the early years of the war, The Dow Chemical Company manufactured several products for France and for other foreign countries-for example, phenol, dinitrochlorobenzene, and other organic compounds. Later in this period the output of phenol reached as much as 40 tons per day. Of particular importance also were the efforts of the company looking toward indigo manufacture, a process for which was finally perfected and the indigo paste actually placed on the market in December, 1916. This was the first indigo synthesis in a large way in America. The advantage of indigo to The Dow Chemical Company lay primarily in the possible utilization of bromine for the preparation of brominated indigos, superior in fastness and brilliance to all other blue dyes save, in some respects, the more expensive indanthrene blues.

Subsequent to the manufacture of phenol by The Dow Chemical Company was the manufacture of salicylic acid and all salicylates. Gradually the company enlarged its pharmaceutical field and entered

also upon the manufacture of certain perfume bases. Furthermore, with a slowly growing demand for metallic magnesium, the company was soon engaged in the preparation of this metal by electrolysis. A small plant for the production of metallic magnesium was in operation by 1918, and sales began in that

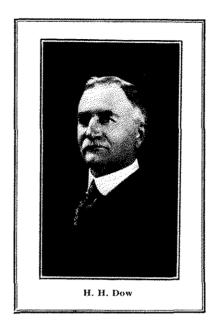
year. The adaptability of this metal in the preparation of a light alloy known as Dowmetal soon demonstrated itself in various ways. The future use of such alloys must undoubtedly figure in aerial transportation.

By 1917 the actual preparation of war material was well under

way. Soon after America's entrance into the conflict, The Dow Chemical Company, operating under government direction, drilled many wells to meet the ever-increasing demand for bromine, especially for the manufacture of tear gases. After considerable work in the Dow laboratories, a process for the preparation of mustard gas from ethylene and sulfur chloride was undertaken on a commercial scale in June, 1918. This proved to be the first commercial production of this material in America.

From a small beginning The Dow Chemical Company has grown as the years have advanced. The scope of manufacture, outside of the simple brine components, has been kept closely within the natural limitations—namely, caustic on the one hand, and halogens on the other. These two types may be portrayed as the guiding lines enclosing the Dow field of chemical endeavor. They take their origin in the Dow electrolytic cell as the vertex of an angle. The utilization to the last moment of all by-products through definite

and interlocking processes secures the field already encompassed. As these lines extend from this vertex, record is steadily made of greater and greater production; and as they diverge from each other ever broader and broader becomes the field of chemical activity.



Concentration by Fractional Condensation

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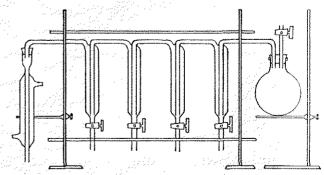
THE apparatus illustrated in the accompanying diagram is of considerable value in helping the student to visualize the vapor-liquid equilibrium that exists when fractionation is possible.

The fractionating bulbs are made from 4×15 cm. test tubes. The inner tubes must reach to within 0.5 cm. of the bottom of the bulbs. A 2-liter flask is used for a boiler and the distillate from the last fractionating bulb is passed into a water-cooled condenser.

For the laboratory experiment, one may start with 1400 cc. of water and 200 cc. of ethyl alcohol in the 2-liter flask, and boil. The first few cubic centimeters of vapor are condensed in the first fractionating bulb and the vapor that follows must bubble through this condensate, causing a richer vapor to pass into the next bulb. The heating of the flask is so regulated that the distillate from the last bulb does not exceed 20 to 30 drops a minute. The fractionating bulbs act as air condensers so that in 30 to 45 minutes they should contain about 30 cc. of liquid. Their contents are then drained into test tubes and the specific gravity determined by either the plummet or hydrometer method. The flame should be allowed to heat the flask until the bulbs are emptied.

Results obtained by over two hundred students using an

apparatus of five bulbs showed 85 to 90 per cent of alcohol in the last bulb with a concentration of 2 to 3 per cent in the first bulb. Although only four bulbs are shown in the figure, a greater number will be more satisfactory if better fractionation is desired.



The results obtained do not, of course, represent equilibrium values, as the equilibrium changes with time of distillation, but they do represent, fairly closely, an equilibrium that exists at the time the distillation is interrupted.

These bulbs will also fractionate other materials, such as kerosene, impure benzene, etc.

1 Received July 2, 1925.