[Contribution from the Department of Chemistry of McGill University.]

SULFURIC ACID CONCENTRATOR AND VACUUM PUMP.

By O. Maass.

Received September 25, 1920.

The sulfuric acid pump here described has been designed for vacuum distillation, and is particularly adapted to the special case where the liquid to be distilled is an aqueous solution which is to be freed, partly or completely, from its water content. When large quantities of solution have to be dealt with, and especially in the case where the formation of appreciable amounts of non-condensible, or of a corrosive gas occurs, the apparatus described in this paper will be found to be very efficient.

The idea occurred to the writer to use the sulfuric acid both as absorbent and evacuating medium, employing the apparatus represented by Fig. 1. The part at the left of O is drawn on a much larger scale and shows how the control which regulates the sulfuric acid pump is connected through Tube O to the latter. A detailed description of the control will be found elsewhere.[1] A′ and A are flasks which act as the containers of the liquid to be concentrated or evaporated. One or both are half filled by suction, the inlet tubes then being sealed off, or closed with ground glass stoppers. G is the sulfuric acid reservoir, and is filled to level "a;" the inlet tube to G is then also closed up. M and F lead to ordinary Geissler suction pumps. The whole system is then pre-evacuated by the Geissler pump leading to F, and when the pressure has fallen to that which the Geissler pump can conveniently establish, the control is started and admits atmospheric pressure to the space above the sulfuric acid in G. The sulfuric acid rushes up through N into B and C, reaching the level "d" in the latter, and driving all the air in D out through the capillary tube at the top of D into E. Finally a portion of the sulfuric acid itself enters E and acts as a seal; then the downward stroke takes place. The control shuts off access of atmospheric pressure to B so that the sulfuric acid is drawn back into G, out of C and D. The weight of the column of sulfuric acid between levels "*b*" and "*e*" is greater than the pressure maintained in E by the Geissler pump. Hence, the sulfuric acid "breaks" at the top of D, and in D there is therefore a perfect vacuum, which is filled with gas and vapor from C, as soon as the sulfuric acid has been lowered into N. C is filled with glass rods, about 3 mm. apart from one another, so that a large surface of sulfuric acid is left in C and absorbs any water vapor coming from A, the non-absorbable gases passing on into D. The next up-stroke of the pump forces these out of D and at the same time renews the surface of sulfuric acid on the rods in C.

Now the following feature of the sulfuric acid pump needs special em-

---

[1] O. Maass, This Journal, 41, 53 (1919).

phasis. Any water vapor which gets into D together with non-absorbable gas is absorbed in the sulfuric acid, while the non-absorbable gas is driven out. When mercury is used, the latter will drive out the gas, but the water vapor condenses during the up-stroke between the walls and the mercury and this water is then vaporized on the down-stroke so that in time the gas pressure in the apparatus will be that of water vapor

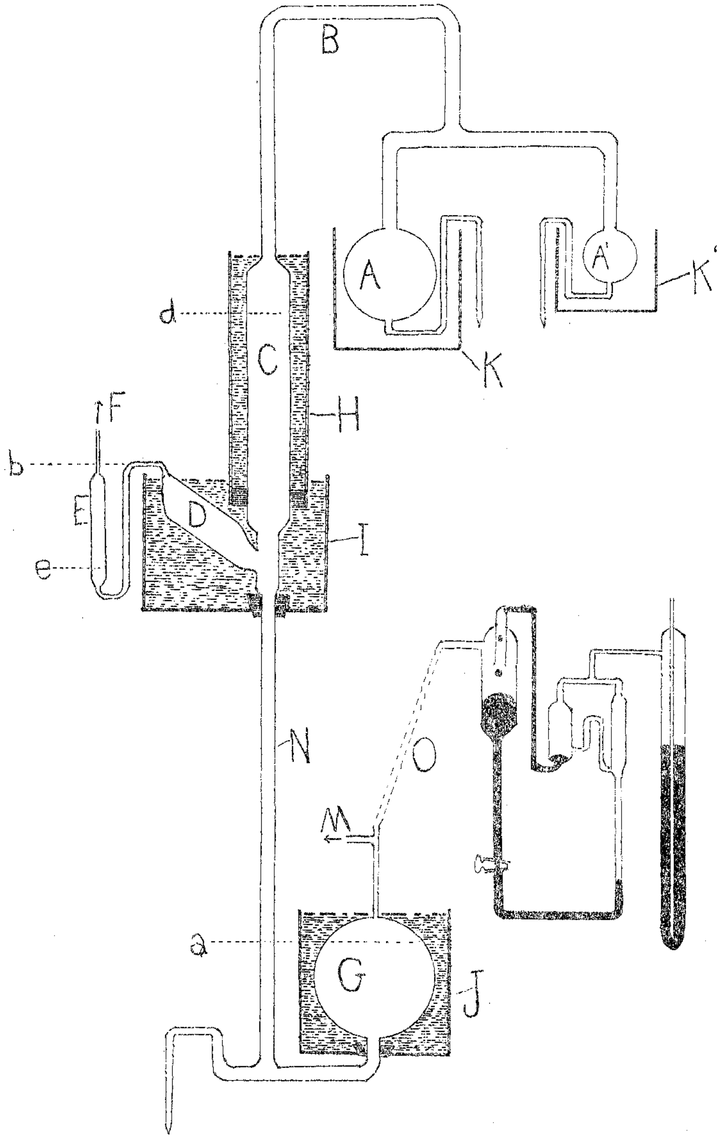

Fig. 1.

at the temperature of the pump. In the case of the sulfuric acid, the pressure will never be greater than that of the vapor pressure of sulfuric acid itself.

C, D and G are water-jacketted to prevent the temperature of the sulfuric acid from rising on account of its water absorption. The circulation of the sulfuric acid is such as to make this quite easy. The acid coming from C is dilute and therefore lighter than that remaining in G, and hence, on entering G, rises to the top. On the next up-stroke the denser acid in G, being at the bottom, enters C first, so that the sulfuric acid is kept thoroughly mixed throughout.

The height of C and D above G can be varied anywhere between 3 and 5.5 meters, the latter being approximately the barometric height in terms of sulfuric acid. The maximum height to which the acid rises is, of course, regulated by the control. The apparatus works automatically so that after being filled and the control having been started, it requires no further attention.

The above suffices to explain the mechanism of the pump, and the next important question to consider is the relation between the temperature at which the concentration is carried out, the time it takes and the amount of acid used up.

In the first pump which was built, Flask A had a volume of 2 liters and was filled with one liter of solution to be concentrated. Sulfuric acid, Reservoir G had a column of 2.5 liters and was filled with 1.5 liters of 95% commercial sulfuric acid. Heat for the evaporation was supplied by the water-bath K, which was heated by a Bunsen burner. As soon as a vacuum was established and the sulfuric acid pump in action, the solution boiled so rapidly that when the temperature of the water-bath was kept at 30°, the temperature of the solution did not rise above 15°.

It was possible, with the aid of the sulfuric acid pump of the small dimensions quoted, to evaporate a liter of water at a temperature of 20° in 3 hours, 1.5 liters of commercial sulfuric acid being required.

Concentrations can be carried out at lower temperatures than 20°; water at 0° boils vigorously. This proved invaluable when highly concentrated hydrogen peroxide solutions were further concentrated, because the low temperature at which it was possible to do so and the small time required prevented any loss due to decomposition.

The following facts may be worth mentioning. When water is placed in A and the pump started without heating the water, the latter supercools and then freezes. The ice formed continues to evaporate and "supercools" itself several degrees below the freezing point. If the pump is stopped and the acid withdrawn into the reservoir and the ice melted, the vacuum above it being maintained during this procedure, then on restarting the pump, the water can be supercooled to an extraordinary degree before it freezes. After repeating this a number of times, the water is de-aerated to such an extent that it evaporates without boiling, the surface remaining absolutely at rest. When freezing finally begins under these conditions, if by chance ice formation starts in the center, beautiful designs appear on the surface. At times the surface is divided into regular hexagons 5 cm. in diameter. Occasionally the water has been supercooled to such an extent that $^3/_4$ of the volume solidified immediately when crystallization started. In no case was the flask broken during the ice formation.

It has been found advantageous to use another form of sulfuric acid pump as a source of vacuum in distillations when the products of the distillation were to be collected. In this case, Portion C (Fig. 1) is dispensed with, as the primary object of the sulfuric acid is to create a vacuum and not to absorb the distillate. The distilling flask is connected to a condensing coil and receiver surrounded by a freezing mixture, a tube of medium diameter replaces C and is connected to the receiver.

In the case where the distillate consists of an aqueous solution, all that has been previously said about the sulfuric acid pump holds; for instance, any vapor getting past the receiver into the body of the pump is absorbed, and therefore does not lower the efficiency of the vacuum. The relatively small density of the sulfuric acid when compared to the density of mercury, makes it possible to make the volume of the body of the pump of such a size that its capacity is comparable to the best rotary pump.

In the case of a larger sized pump, the latter is best constructed out of lead, and the Geissler pump used for "driving purposes" replaced by an electric pre-evacuator.

In some recent work on tar sands carried out by Dr. Krieble and Mr. Seyer at McGill University, it was found that in the fractional distillation of oil extracted from tar sands cracking could only be avoided by distilling under as low and as constant a vacuum as possible. Various vacuum pumps which were tried, failed to give the desired result principally because part of the oil consisted of volatile constituents which found their way past cooling coils and reduced the efficiency of the particular pump used. The sulfuric acid pump proved adequate, as the volatile portions were absorbed by the sulfuric acid without a change in the vacuum being noticeable and the vacuum could invariably be maintained for any length of time desirable.

The preparation of pure hydrogen peroxide on a large enough scale was rendered possible only by the sulfuric acid concentrator and the sulfuric acid pump described above.

MONTREAL, CANADA.