

was shown that without exception all of the bactericidally effective aliphatic acids were marked surface tension depressants. Several general correlations between chemical structure and surface tension depressant action were revealed.

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STUDIES OF POLYMERIZATION AND RING FORMATION. XI. THE USE OF MOLECULAR EVAPORATION AS A MEANS FOR PROPAGATING CHEMICAL REACTIONS

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Reversible reactions involving the simultaneous formation of a volatile and a non-volatile product are often forced to completion by causing the volatile product to distil from the reaction mixture as fast as it is formed. The purpose of the present note is to call attention to the possibility of extending the application of this principle to instances in which the effective vapor pressure or escaping tendency of a volatile product or potential product is very small. In the molecular still¹ distillation or continuous evaporation can be effected even when the vapor pressure of the distilling substance is as low perhaps as 10^{-5} mm. The theory of the process has been discussed by Washburn,^{1b} and we need only to mention that successful operation requires a highly evacuated system comprising a condenser placed very close to the evaporating surface. The temperature of the condenser must be low enough to reduce the vapor pressure of the distillate to a negligible value. Under these conditions the mean free path of the molecules is less than the distance from the condenser to the evaporating surface; consequently most of the molecules that manage to escape from the evaporating surface are caught by the condenser with a negligible probability of return.

Mercury and apparently cane sugar can be evaporated in the molecular still at room temperature^{1b} and *n*-heptacontane can be distilled without decomposition.² The tendency to distil diminishes with increasing molecular weight, and it appears that, so far as practically useful rates are concerned, the upper limit of distillability for paraffin hydrocarbons may lie at as low a molecular weight as 1100 or 1200. For other types of organic compounds it will in general lie at still lower molecular weights.² Thus all substances of high molecular weight are practically completely

¹ Brönsted and Hevesy, *Phil. Mag.*, **43**, 31 (1922); (b) Washburn, *Bur. Standards J. Research*, **2**, 476 (1929); (c) Burch, *Proc. Roy. Soc. (London)*, **123**, 271 (1929); (d) Hickman, *Chem. Ind.*, **48**, 365 (1929).

² Carothers, Hill, Kirby and Jacobson, *THIS JOURNAL*, **52**, 5279 (1930).

non-volatile. There are many instances of reversible reactions in which only one volatile substance is involved. If this substance has a very low vapor pressure, or if it is strongly held by other substances involved in the reaction, or if its equilibrium concentration is very low, then molecular evaporation may be capable of producing a result not even remotely accessible with the aid of the usual distillation equipment and methods.

Examples of the use of molecular evaporation as a means of propagating chemical reactions are provided in other papers of this series.³ The reactions involved are reversible bifunctional condensations. The starting materials are linear polymers capable, by self-combination, of yielding a still longer molecule with the elimination of some volatile product. The size of the product molecules depends upon the completeness of the reaction. With the aid of the molecular still one can obtain products of much higher molecular weight than with the ordinary distillation equipment. The same principles can doubtless be applied to other kinds of reversible reactions.

The simple stills described by Washburn,^{1b} function satisfactorily but they do not provide ready access to the residue from the distillation. For this reason we constructed the instrument shown in Fig. 1 and used it in carrying out some of the reactions referred to above. The new instrument has the advantage that the flat pan containing the distillation residue can be lifted out when the instrument is open.

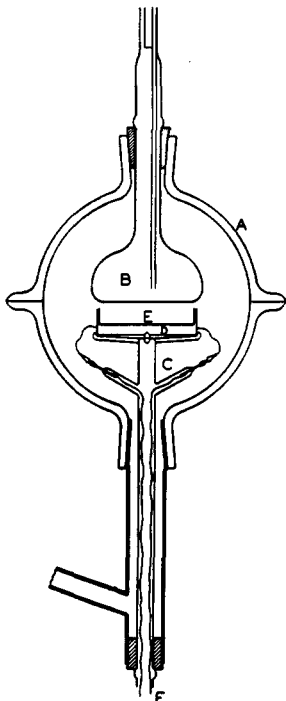


Fig. 1.—Molecular still ($1/7$ natural size).

The outer shell (A) of the apparatus is made up of two domes from Pyrex vacuum distilling apparatus (Corning Glass Company Catalogue, Item No. 56). The ground surfaces are lubricated with a good vacuum grease. (B) is the condenser provided with water leads. (C) is the glass support for the heater (D) and the distilling pan (E).⁴ The heater and distilling pan are contained in an outer copper pan as shown. The heater consists of nichrome wire wound spirally on a sheet of mica which is supported between sheets of thin asbestos

³ Papers XII, XIII, XIV and XVI.

⁴ This pan is conveniently made by cutting a Pyrex beaker close to the bottom. The material of which the pan is composed has a considerable effect on the rate of the bifunctional condensations described in Papers XII, XIII and XIV. No polyesterification could be effected in a copper pan. On the other hand, when superpolyesters and polyanhydrides are prepared in a glass pan the products adhere very firmly to the glass so that the dish is frequently shattered on cooling owing to the force of contraction.

board inserted below the distilling pan. The heater leads (F) are brought up through the support (C) and out as shown. Connection with the heater is made with spring clamps which make the heater readily demountable. The lower part of the apparatus is the regular distilling tube provided with the Pyrex vacuum distilling apparatus (Catalogue No. 56). The rubber stoppers at the top and bottom of the apparatus are well covered with a suitable wax such as picein. A thermocouple (not indicated in the drawing) is led in through the lower wax seal and the junction placed under the pan (E). The slight bulges on the condenser and the pan support where they enter the apparatus are necessary to obviate the danger of these parts sucking in when the apparatus is evacuated.

Summary

In reversible reactions involving the simultaneous formation of volatile and non-volatile products, the use of molecular evaporation makes it possible to realize chemical effects that cannot be achieved with the aid of the usual distillation equipment. A new design of molecular still is described.

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STUDIES OF POLYMERIZATION AND RING FORMATION. XII. LINEAR SUPERPOLYESTERS¹

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In previous papers we have described polyesters having molecular weights ranging from 800 to 5000 derived from dibasic acids of the series $\text{HOOC}(\text{CH}_2)_x\text{COOH}$ and glycols of the series $\text{HO}(\text{CH}_2)_y\text{OH}$.² These esters are microcrystalline solids that dissolve readily in appropriate solvents. Their solutions are not highly viscous and they show no signs of inherently colloidal behavior. In the present paper we describe polyesters of the same series having much higher molecular weights. They exhibit colloidal behavior and simulate to a remarkable degree some of the properties of certain naturally occurring high polymers. For the sake of brevity and convenience we use the designation α -ester or α -form for the polyesters having molecular weights ranging from 800 to 5000 and the designation ω -ester or ω -form for the new superpolyesters.

Nature of the Polyesterification.—The mutual esterification of dibasic acids and dihydric alcohols is a bifunctional reaction.³ As such it presents

¹ The term "superpolymer" is applied to linear polymers having molecular weights above 10,000.

² (a) Carothers and Arvin, *THIS JOURNAL*, **51**, 2560 (1929); (b) Carothers and Van Natta, *ibid.*, **52**, 314 (1930); (c) Carothers and Dorough, *ibid.*, **52**, 711 (1930); (d) Carothers, Arvin and Dorough, *ibid.*, **52**, 3292 (1930).

³ Carothers, *ibid.*, **51**, 2548 (1929).