6. Selective separating processes

By this term we denote processes in which, as the result of the addition of a substance or substances in the gaseous, liquid or solid state, a distillative separation is favourably affected (or sometimes even rendered possible). The term also includes procedures involving a reaction that gives rise to new substances, which are removed by the distillation in the same operation. Furthermore it can be taken to cover methods which by a combination with another procedure, for instance chromatography, supplement the process of distillation in specific cases.

According to Gibbs' phase rule a completely soluble binary mixture is enriched in both phases, whilst an immiscible binary mixture, with its three phases, cannot be enriched (see Fig. 29, a—d). It will be recognized, on the other hand, that three-component systems having a miscibility gap, *i.e.* showing two liquid phases and one vapour phase, are separable by countercurrent distillation [1]. A typical example is the preparation of absolute alcohol by azeotropic distillation with benzene.

6.1 Carrier vapour distillation

The most familiar example of carrier vapour distillation is the distillation of high-boiling materials *with steam*. The use of a carrier vapour has the double object of separating the volatile from the non-volatile components with a reduction in boiling point, and of thereby avoiding thermal decomposition. The process takes place under conditions comparable with those existing in vacuum distillation. The volatile substance passes over at an effective pressure p_1 that is lower than the total pressure p_{ges} of the system. The difference $p_{ges}-p_1$ is the partial pressure p_2 of the carrier vapour. In normal distillation at a reduced pressure it is necessary either to increase the temperature or to reduce the pressure during the course of the distillation. In steam distillation the same effect is obtained by an (automatic) increase in the proportion of water vapour [2].

Steam distillation is particularly valuable for purifying and separating substances partially or totally insoluble in water, such as ethereal oils, fatty acids, fatty alcohols, aniline, tallow oil, waxes, fractions of petroleum and tar etc. A further advantage of this process is that the steam displaces atmospheric oxygen and hence protects the material from oxidation. Steam distillation is much used in preparative work for dealing with gummy or alkaline reaction products.

As has been pointed out in section 4.3 and 4.5, the two components in steam distillation behave as though each of them were present alone at the existing temperature, provided they are immiscible. The total pressure acting on the boiling mixture

is the sum of the partial pressures of the components, one of which is water. The partial pressures and the boiling point of the mixture may be determined, as described in section 4.5 by means of the additive formula. A more convenient procedure is to draw a diagram according to the method of Badger and McCabe [2]. In this diagram one first plots the vapour pressure curves of the substances to be distilled (Fig. 218). Next, one draws curves for the values of the total pressure minus the vapour pressure of water. For instance, water has a vapour pressure of 150 mm at 60.1 °C; thus for the curve for atmospheric pressure one plots 760 − 150 = 610 mm against 60.1 °C.

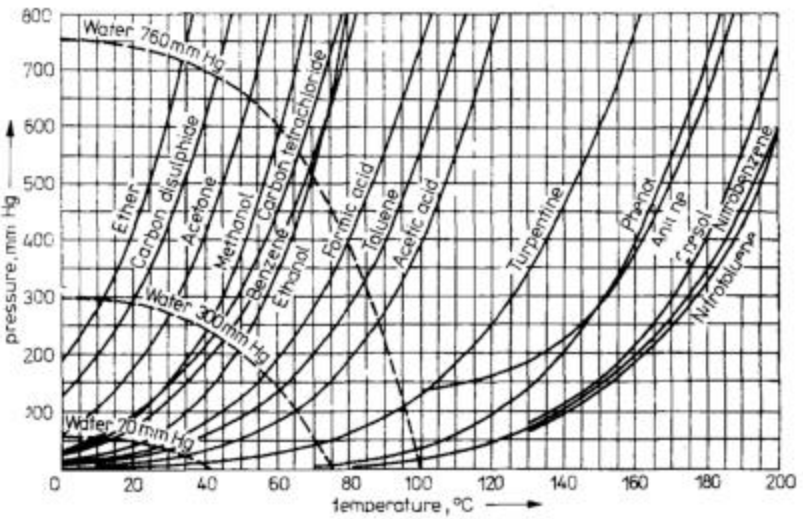

Fig. 218
Diagram for determining the boiling point and the partial pressures in steam distillation (Badger and McCabe)

The point of intersection of the latter curve with that for the vapour pressure of the substance gives the temperature of the mixed system and the partial pressures of the components. (The diagram is sometimes drawn on a logarithmic scale.)

From the partial pressures, the vapour composition can be calculated by formula (40). The proportion by weight of the component to carrier steam is determined by

$$\frac{G_1}{G_2} = \frac{p_1 M_1}{p_2 M_2}. \tag{191}$$

For the mixture toluene-water we thus find

$$\frac{G_1}{G_2} = \frac{337 \times 92}{423 \times 18} = 4.1 \tag{192}$$

which signifies that to distil 4.1 kg of toluene we require 1 kg of water vapour. By formula (40) we find that the toluene content of the mixture is 80.3% wt. and from Fig. 218 it is seen that the boiling point of the mixture is 84.4 °C.

Readily decomposable compounds may be distilled with steam at a reduced pressure. From Fig. 218 we see, for example, that the mixed boiling point of aniline-water, which is 98 °C at a total pressure of 760 mm, falls to 75° if this pressure is 300 mm; it is assumed, of course, that only enough steam for saturation is blown in. Steam distillation at a reduced pressure is desirable for distilling substances with low vapour pressures (such as fatty acids of high molecular weight) and for dealing with mixtures containing a component in low concentration (for instance oils containing traces of a solvent).

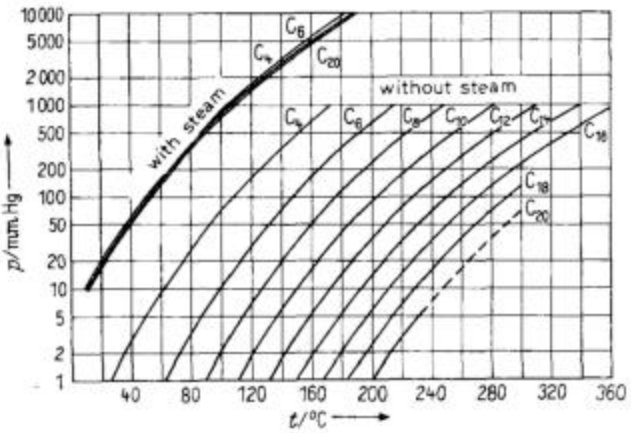

Fig. 219
Boiling points of the straight-chain, saturated, even-numbered fatty acids, with and without steam, as a function of the distillation pressure

The results of using *superheated steam* — which is widely employed in industry for the distillation of tars, mineral oils, fatty acids, glycerin etc. — have been critically discussed by Stage. Taking the saturated C_4 to C_{20} straight-chain fatty acids as an example, he showed that when using saturated steam boiling points are depressed by about 160—240 deg. C, but that at the same time the differences in boiling point, from member to member, became so small that a separation into individual compounds was then impossible (Fig. 219). If, however, the separation was performed with 10% of superheated steam at a pressure of 10 mm, the differences in boiling point remained unaffected and the inherent advantages of steam distillation (good mixing and absence of local superheating) were still present; the average reductions in the temperature, on the other hand, amounted to only 20 deg. C [3]. It may be pointed out that mixtures of fatty acids and fatty alcohols can also be separated reasonably well in stages by steam distillation coupled with partial condensation [4].

Although steam is the carrier vapour most used, on account of its low molecular weight, its high heat of evaporation and the ease with which it is condensed, other gases also find application in industry for effective pressure reduction. In the production of hard coal tar pitch, for instance, waste gases containing CO_2, N_2 and water

vapour are employed as carriers [6]. The presence of inert gas does not cause any appreciable reduction in column efficiency [7]. A graphical method for calculating the condensation of steam-gas mixtures was evolved by Algermissen [8].

Apparatus for carrying out steam distillation can be put together without difficulty from ordinary laboratory components. Fig. 220 shows a set-up for distilling with saturated steam at atmospheric and reduced pressures. The flask *a* is thoroughly insulated with glass wool, or slag wool; it is advisable to heat it as well, in order to prevent the condensation of water. The steam inlet *b* is provided with a cock for

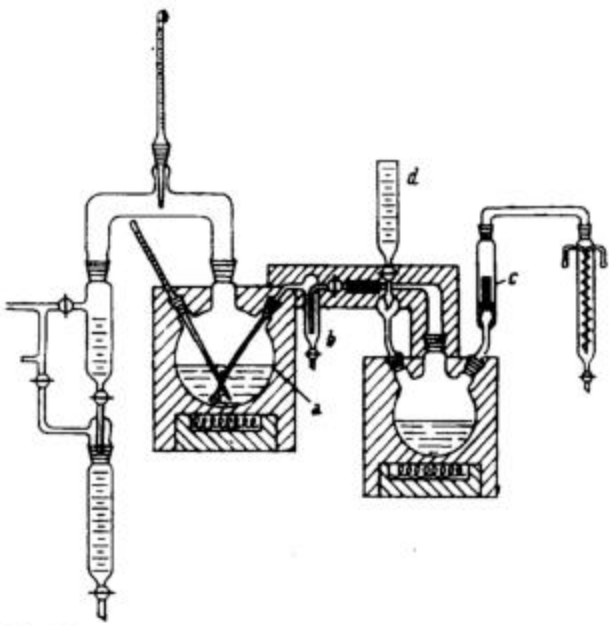

Fig. 220
Arrangement for distillation with saturated steam

drawing off condensed water and can also be employed for passing in other carrier gases. Fig. 221 illustrates the method of distilling with superheated steam in countercurrent operation. The steam is produced in a metal boiler *a*, equipped with a sight glass. Superheating takes place in the cónical metal spiral tube *b*, which is connected to a water trap and a thermometer. It is advisable to include a safety valve in the steam line. An arrangement developed by Tropsch [7] has also proved suitable for superheating. For comparative experiments it is necessary to supply the steam in constant, measurable amounts. A simple method of regulating the amount is shown in Fig. 220 where water is admitted dropwise from the graduated cylinder *d* into the steam boiler, care being taken to maintain a constant level. A more accurate method is that described by Merkel [9], who regulates the amount of steam by the pressure produced in one limb of a manometer. A steam production unit has been developed by Stage et al. [10] to an arrangement in which the steam can be accurately measured.

Water is admitted continuously from a measuring burette into the heated apparatus, which is filled half full with sand to promote heat transfer. Alternatively the water may be evaporated in a coil immersed in a metal bath.

For the distillation of small amounts of material the apparatus of Pozzi and Escot [11] is very convenient, as the steam-boiler simultaneously serves as heater for the distillation vessel (Fig. 222). Parnass and Wagner [12] offer an arrangement for microscale work.

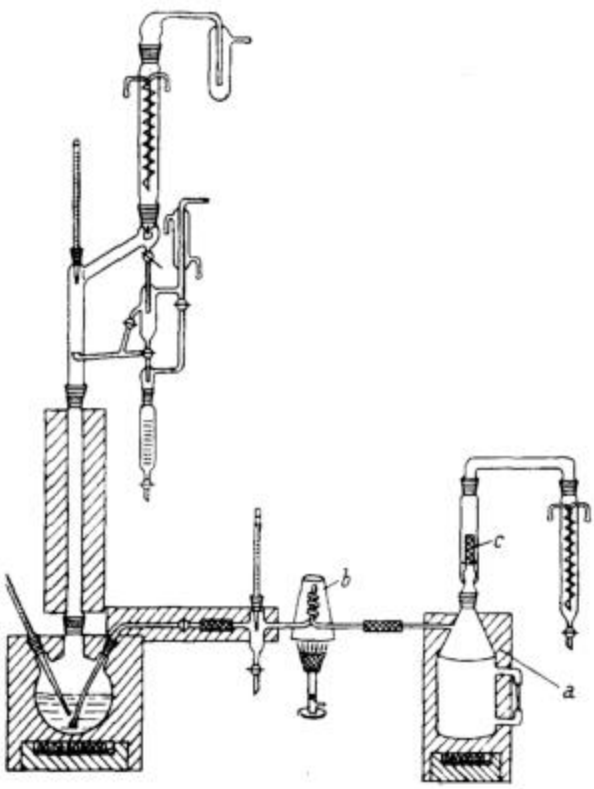

Fig. 221
Arrangement for distilling with superheated steam in countercurrent operation

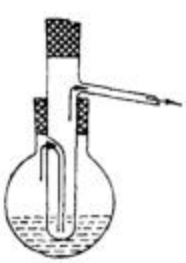

Fig. 222
Device for the distillation with steam of small amounts of material (Pozzi and Escot)

The methods of steam distillation have been summarized by Bernhauer [13] and Thormann [14]. A detailed discussion of practical and theoretical aspects of steam distillation as illustrated by the distillation of essential oils is given by von Weber [15]. Rigamonti [16] developed a nomogram which can be used to calculate the steam requirements for various enrichments. Prenosil [16a] compared theoretical and experimental steam distillation data for multicomponent mixtures. He modified the calculating method by introducing a value for evaporation efficiency. Steam distillation can also be carried out in thin-film apparatus. Berkes et al. [16b] give a description of the material transfer conditions of a steam distillation performed in such apparatus in terms of the balance equations.

6.2 Azeotropic and extractive distillation

Whilst azeotropic and extractive distillation are now employed extensively for difficult separations on an industrial scale [5], it has been usual in the laboratory to resort to other processes, such as extraction and chromatography, for separating narrow-boiling and azeotropic mixtures. It will be shown below that under unfavourable conditions selective processes, such as azeotropic and extractive distillation, offer considerable advantages. The common characteristic of the two is that the ratio of the activity coefficients of the components is influenced by adding another substance [17]. A combination of the two processes termed azeotropic-extractive rectification was proved to be feasible by Künnerle [18]. Gerster [19] compared these selective processes with ordinary distillation from the point of view of economy.

A comparison between extraction and extractive distillation for the purpose of separating aromatic hydrocarbons from petrol produced by pyrolysis and reformate was made by Müller [19a]. He shows in which cases extraction and in which extractive distillation is advantageous, including the economical aspect. Helms and John [19b] have described the extractive distillation of aromatic hydrocarbons by the "Lurgi-Distapex" method. They used n-methyl pyrolidone (NMP). The purities obtained were 99.95, 99.7 and 99.8% for benzene, toluene and xylene, respectively. The book of Hoffmann [5] which contains numerous calculations for binary, ternary and multicomponent systems offers a thorough treatment of the problems associated with azeotropic and extractive distillation. Results of laboratory experiments on the separation of strongly non-ideal mixtures by means of azeotropic and extractive distillation as exemplified by the distillation of acryl nitrile are reported by Schober et al. [19c]. In addition, the authors have made a theoretical study of mixtures of HCN, acryl nitrile, acetonitrile, oxazole, H_2O.

In the case of *non-ideal mixtures* without a special point the equilibrium curve approaches the diagonal asymptotically at the upper or lower end (for examples see Fig. 29f and h). Even with relatively great differences in boiling point between the components a separation of such mixtures requires a considerable number of separating stages. Mixtures having a special point (azeotropes) give the following results when submitted to countercurrent distillation with sufficient separating power.

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Chapter 6 — Selective Separating Processes

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