U.D.C. 543.212

# Methods of Measurement of Small Separation Coefficients

D.A.Knyazev, Ya.D.Zel'venskii, N.F.Myasoedov, and G.G.Filippov

Methods of measurement of small separation coefficients are reviewed. The methods cover the whole range of separation conditions used in practice. Their main characteristics are tabulated, and each method is discussed mathematically in detail. The limitations of their applicability are considered, together with the magnitude of likely sources of error. The preferred regions for the various methods are identified, specific features of the experimental procedure are listed, and the apparatus is described. Most of the examples are taken from papers on the separation of isotopes, because this work demands the highest precision and reliability in the measurement of separation coefficients, and offers the widest choice of published results. 87 references.

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## I. INTRODUCTION

A new and fast-developing area in chemical engineering and in preparative and analytical chemistry is concerned with the separation of mixtures of closely similar constituents. Systems of this type include many mixtures of biologically important substances, such as mixtures of aminoacids and of polysaccharides, mixtures of members of genetic and of homologous series, of polymers, of isomers, of isotopes, of rare earths, etc., all of which are notoriously difficult to separate.

The thermodynamic properties of these compounds are usually very similar over a wide range of conditions and for the most diverse chemical forms and states of aggregation into which they can be transformed. Hence the difficulty experienced in separating them. The corresponding separation processes (or reactions) are characterised by single-stage separation factors close to unity, and therefore methods which automatically perform a multiplicity of separation acts are used to prepare the pure compounds. The most important of these methods are fractional distillation, extraction, chromatography, fractional crystallisation, and their many variants.

The rational application of these processes demands a knowledge of the separation coefficients of the components in the particular physicochemical systems under study. This is clearly recognised in the area of isotope and rare-earth separation, and one of the main research activities with these materials is a search for systems and conditions giving rise to significant or acceptable separation coefficients. On the other hand, in biochemistry and related areas the approach tends to be empirical, and preliminary studies of the magnitude of the elementary act are usually omitted. There can be no doubt that a more quantitative approach is needed in this area also, involving a sufficiently accurate analytical assessment of the efficiency of the process under study.

The methods most frequently used to determine separation coefficients are listed in Table 1 together with a brief summary of their main characteristics.

### Definitions

The term "small separation coefficient" is used to denote values close to unity, but the extent of approach to unity is not defined. It may be convenient to include all value not exceeding two, because their measurement requires the use of high-precision methods such as those discussed in this review. These special methods must be used also when the separation coefficients being measured differ fractionally from unity: hence there is a similarity between very small separation coefficients and those of the order of two.

Separation coefficient. Given two chemical forms, phases, or states A and B between which the components $i$ and $l$ can undergo chemical or phase exchange, the separation coefficient $\alpha_{il}$ which characterises the exchange of the components is defined by

$$\alpha_{il} = \frac{[x_i]_A}{[x_l]_A} \cdot \frac{[x_l]_B}{[x_i]_B}$$

where $[x_i]_A$, $[x_l]_A$, $[x_i]_B$, and $[x_l]_B$ are the mole fractions of the components in forms A and B respectively. Both equilibrium and non-equilibrium process can be characterised by means of $\alpha$. In the former case the concentrations must meet the usual requirements of dynamic equilibrium. The following terms are often used synonymously with separation coefficient: single-stage separation factor, equilibrium constant, relative fugacity.

The *enrichment coefficient* is defined by the expression

$$\varepsilon_{il} = \alpha_{il} - 1.$$

The value of $\epsilon$ for mixtures which cannot be easily separated is often much smaller than unity, and in these cases the separation obtainable in the system is best described in terms of $\epsilon$. This quantity will therefore be used most frequently in what follows, and the precision of the experimental methods will be referred to it.

**Table 1.**

| Method | Single contact | Differential | Multistage extraction | Rayleigh's continuous extraction | Elution chromatography | Rectangular cascade | Craig counter-current extraction |
|---|---|---|---|---|---|---|---|
| Field of application / Characteristics | Heterogenous phase exchange | Phase exchange | Heterogeneous exchange | Heterogeneous and homo-geneous phase exchange | Heterogeneous exchange | Heterogeneous phase exchange | Heterogeneous exchange |
| Lowest measurable values | 0.03 | 0.005 | 0.002 | 0.002 | 0.0002 | 0.01 | 0.01 |
| Amount of mixture (mmole) needed | 0.1—10 | 5—20 | $10^2$—$10^4$ | $10^2$—$10^4$ | $10^{-2}$—$10^{-1}$ | $10^4$ | $10^{-1}$—1 |
| Number of precision analytical determi-nations per measure-ment | 2 | 0 | 2 | 2 | 10 | 2—10 | 10 |
| Duration of experiment ignoring preparative stages | minutes to hours | minutes to hours | over an hour | hours | hours to days | hours to days | hours to days |

Degree of separation. The efficiency of any separation process operated in an apparatus designed to maximise the effect of single-stage separation is characterised by the degree of separation, which is generally referred to the initial and the final state of the product, to some fixed points in the apparatus, and to a specified time:

$$Q_{il} = \frac{[x_i]_1}{[x_l]_1} \cdot \frac{[x_l]_2}{[x_i]_2}.$$

The time parameter needs to be considered only in special cases, and is therefore often omitted in the definition of $Q_{il}$.

## II. SINGLE CONTACT METHOD

The field of application of the single contact method embraces all types of physicochemical equilibrium. The method is used to measure small coefficients when only a preliminary assessment is required, or when the result is sufficiently different from unity to ensure that the desired precision is achieved without resorting to multiple separations. In this case the problem consists in measuring the concentrations of the materials in the phases or forms to be equilibrated. The measurement accuracy can be improved by a number of simple procedures, by the use of special analytical methods, or by taking a large number of measurements and applying a standard statistical analysis.

If a method for measuring the difference in concentration of components $i$ and $l$ in the forms to be equilibrated is available, and the concentration of the components in the initial mixture is accurately known, the coefficient $\epsilon_{il}$ for the multicomponent mixture can be determined from the expression

$$\varepsilon_{il} = \frac{x_l^0 \Delta i - x_i^0 \Delta l}{(x_i^0 - \theta \Delta l)\left[x_l^0 - (1-\theta)\Delta i\right]} \qquad (1)$$

where $\Delta i = x_i - y_i$, $\Delta l = x_l - y_l$, $x_i^0$ and $x_l^0$ are the initial concentrations of the components $i$ and $l$, and $\theta$ is the fraction of the material in form B, for which the concentrations are denoted by the symbol $y$.

In the case of a binary mixture the expression can be simplified, and only the concentration difference $\Delta_1$ of the first component and the quantity $\theta$ need to be measured:

$$\varepsilon = \frac{\Delta_1}{(1 - x_1^0 - \theta\Delta_1)(x_1^0 - \Delta_1 - \theta\Delta_1)}. \qquad (2)$$

It is often possible and desirable to contact small amounts of form B with large amounts of form A. In this case $\theta \to 0$, and the measurement of $\epsilon$ involves simply a measurement of the difference $\Delta_1$:

$$\varepsilon = \frac{\Delta_1}{(1 - x_1^0)(x_1^0 - \Delta_1)}. \qquad (3)$$

It is evident from the above expressions that, other conditions being equal, the value of $\Delta_i$ and $\Delta_l$ increases with $x_l$ and $x_i$. Since the accuracy of the measurement of $\epsilon$ is determined by the accuracy with which $\Delta$ can be measured, conditions tending to maximise $\Delta$ should obviously be chosen if possible.

The relationship between the accuracy of the measurement of $\epsilon$ and that of the analytical method used is illustrated by the highly precise work of Boato and coworkers [1], who studied the separation of nitrogen, oxygen, and noble gas isotopes by liquid–vapour phase exchange. Due to the small error of their mass-spectrometric method of analysis, they were able to measure $\epsilon$ to the fourth decimal place.

The experimental requirements of the single contact method are determined primarily by the nature of the separation process under study. In the case of equilibrium separation processes the requirements coincide with the well known conditions for the achievement of true dynamic equilibrium. The most important of these is a correct choice of equilibration time, which implies a fairly precise knowledge of the kinetics of the process. The equilibrium criterion most commonly adopted is agreement between

values of $\epsilon$ obtained after long and significantly different contact times, or after approaching equilibrium from different directions.

In the study of non-equilibrium separation processes, on the other hand, we must ensure that the reaction can proceed in one direction only. This is most frequently achieved by working on the initial portion of the relaxation curve or under artificially maintained quasi-stationary conditions. For example, in high-vacuum distillation studies the molecules emitted from the liquid at a given temperature must be condensed at a very much lower temperature to ensure that the backward flow of molecules is negligibly small.

The apparatus required for the single contact method is usually fairly simple. Typically, temperature-control and stirring facilities are needed. The apparatus and techniques used in extraction, crystallisation, and ion exchange studies have been discussed in recent review articles [2-4]. The monograph by Hala and coworkers [5] gives an extensive and detailed review of the experimental assemblies used to study liquid–vapour equilibria. Apparatus based on Bushmakin's design [6] is most commonly used in Soviet laboratories investigating liquid–vapour equilibria. Combs and coworkers have proposed a contact apparatus which ensures complete saturation of the carrier gas by the vapour. More complicated designs are used in studies of non-equilibrium processes or under extreme experimental conditions. For example, the apparatus for studying separation by high-vacuum distillation has some unusual design features [8].

## III. DIFFERENTIAL METHOD

The differential method [9,10] applies only to the liquid–vapour phase transition in binary mixtures, since it relies on the difference in equilibrium vapour pressure of two liquids at the same temperature, or alternatively on the difference in boiling point at a fixed pressure. There is a simple relationship between these easily measurable quantities and the separation coefficient, due to the similarity in thermodynamic properties of substances which are difficult to separate, which ensures that liquid and gaseous mixtures of this type are thermodynamically ideal. At a constant temperature, the vapour pressure of an ideal binary liquid mixture is the sum of two partial pressures which are themselves determined (according to Raoult's law) by the composition of the liquid mixture in equilibrium with the vapour:

$$P = P_1^0 x_1 + P_2^0(1 - x_1); \quad y_1 = \frac{P_1^0 x_1}{P}; \quad y_2 = 1 - y_1 = \frac{P_2^0(1 - x_1)}{P}. \quad (4)$$

The separation coefficient of the equilibrium distillation process is

$$\alpha = \frac{y_1}{y_2} \cdot \frac{x_2}{x_1} = \frac{P_1^0}{P_2^0} = 1 + \frac{P_1^0 - P_2^0}{P_2^0}. \quad (5)$$

The measurement of $\alpha$ involves merely a determination of the difference in vapour pressure between the two liquids ($\Delta p$) [9,11] and of the absolute vapour pressure of one of the liquids (isothermal variant). The same problem can be solved indirectly by measuring the difference in boiling point between the liquids as a function of pressure, and also the vapour pressure of one of the liquids as a function of temperature (isobaric variant [10]). The method can be used also to test the ideality of mixtures [12] or to study the variation of $\alpha$ with composition of the liquid phase [13]. In this case the vapour pressure of a series of mixtures is measured with respect to that of a standard mixture, or of a pure component. *A priori* evidence of the ideality of the mixture is often available, as in the case of mixtures of isotopic forms, of isomers, or of near homologues. In these systems, a relative measurement of the vapour pressure of two mixtures of known and different composition is sufficient to determine $\alpha$. The quantities $P_1^0$ and $P_2^0$, and therefore also $\alpha$, are obtained by solving the simple system of simultaneous equations

$$P' = P_1^0 x' + P_2^0(1 - x')$$

$$P'' = P_1^0 x'' + P_2^0(1 - x''). \quad (6)$$

The same information can be obtained by measuring differences in boiling point. The isobaric (ebullioscopic) method involves the determination of $\Delta t$ as a function of total pressure in order to arrive ultimately at expressions (4)–(6). The mathematical transformation is performed graphically or by means of empirical expressions.

These two methods offer a number of advantages over alternative methods of measuring small values of $\epsilon$. The apparatus and procedure are relatively simple, no special analyses are required, the parameter $\alpha$ can be measured over a very wide range of temperatures and pressures, and as a function of composition, and lastly very small amounts of material are needed for the measurement, and can be recovered. The main drawback of the method is the requirement of extreme purity, since both modifications of the method are very sensitive to the presence of volatile impurities. The isothermal modification has the advantage that measurements of $\Delta p$ as a function of temperature are not normally required, but there is little to choose between the two variants when measurements of $\alpha$ are required over a fairly wide range of conditions.

The method has become generally used [9-11,13-16] as one of the most reliable procedures for measuring $\alpha$ in isotopic mixtures. It has also been applied to mixtures of isomers [12] and to non-ideal mixtures [13].

The main parts of an isothermal apparatus for the measurement of $\alpha$ by the differential method are a manometer to indicate the pressure of the substances or mixtures to be compared, a differential manometer, a temperature control system, a vacuum system, and a gas-handling system (Fig. 1). In the best designs, the manometers are in the form of holes drilled through metal blocks of high thermal conductivity in order to minimise temperature differences and to increase the thermal inertia of the system [14]. Constructions have been described which allow the temperature to be controlled to 0.0001° at the −195°C level, and to 0.01° at +370°C. [15,15a,16]

Combs and coworkers [7] used an unusual form of the differential isothermal method. A stream of carrier gas is led alternatively through thermostatted saturators containing the liquids to be compared and through desorbers. The design of the saturators and desorbers ensures quantitative saturation and scrubbing: the vapour pressure of the liquids is measured by the increase in weight of the desorbers.

Isobaric assemblies are based on ebulliometers essentially similar in design to the device described by Hala and coworkers [5]. The only difference is that two ebulliometers are used together, in a common manometric system.

The accuracy of the method is controlled by the following factors: the absolute difference in vapour pressure or in boiling point of the substances being compared, the precision of the equipment used to measure $\Delta p$ or $\Delta t$, the

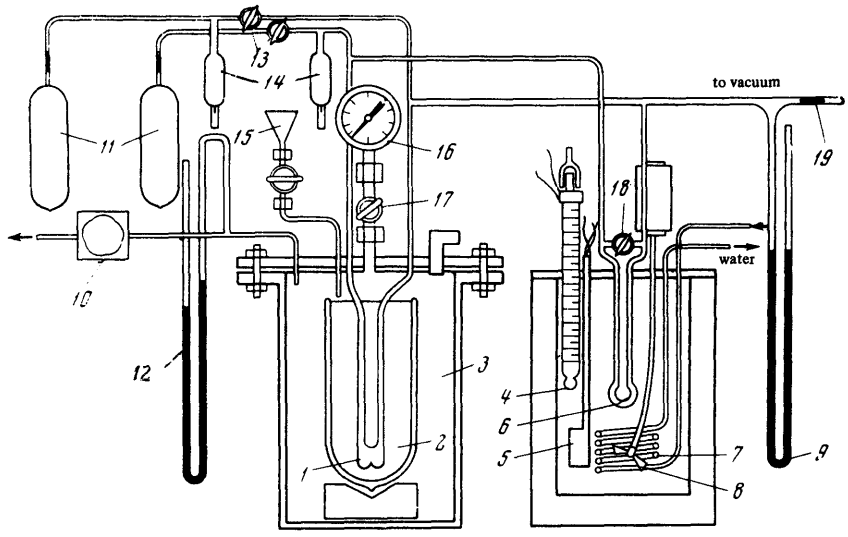



**Figure 1.** Apparatus for measuring $\alpha$ by the differential method: *1*) bulb for experimental liquid; *2*) Dewar vessel; *3*) metal jacket; *4*) contact thermometer; *5*) heater; *6*) differential manometer; *7*) cooling coil; *8*) stirrer; *9*) mercury manometer; *10*) needle valve; *11*) storage bulbs; *12*) vacuum gauge; *13*) taps; *14*) sample holders; *15*) filler tap and funnel; *16*) manometer; *17*) valve; *18*) manometer bypass valve; *19*) vacuum seal-off point.

grade of the thermostat or manostat, and the purity of the compounds. Differential manometers are usually read with a cathetometer, which allows $\Delta p$ to be measured with a precision of 0.01 mmHg. In principle, therefore, it is possible to measure $\epsilon$ with an error of a few units in the fifth decimal place. The isobaric method is more complicated and not so widely used. It requires specially calibrated resistance thermometers and a special electrical measuring bridge. The measurement accuracy can be as high as 0.001°, and the error in $\epsilon$ can be of the same order as in the isothermal variant.

Purity of the samples to be compared is the overriding condition for a successful and accurate determination of $\epsilon$. To achieve the requisite purity, a complex sequence of purifications is often required, involving the development of special procedures and apparatus.

## IV. MULTISTAGE EXTRACTION (CONDENSATION) METHOD

The multistage extraction method consists in the gradual enrichment (with respect to one or several components) of one of the two forms, achieved by simple repetition of a single-stage separation procedure. The experimental pair of chemical forms A and B is brought into dynamic equilibrium, the mixtures in form A and B respectively being taken in comparable amounts. Forms A and B are separated before the establishment of equilibrium: one of these forms becomes enriched with respect to one of the components, and vice versa. The entire operation (equilibration and separation of the forms) is termed a condensation stage. After the first stage, some fraction of form (or phase) A is converted into form (or phase) B by chemical or thermal methods. The sample of form B thus obtained, and the remainder of form A, are then brought into dynamic equilibrium once again, and forms A and B are again separated. As a result of the second stage, form A is enriched still further in the given component, and the subsequent "condensation" stages of form A raise the level of separation of the components to the point when the separation of all the components becomes accurately measurable. The degree of separation is measured with respect to the concentration of the components in form A after the first "condensation" stage. The amounts of forms A and B are controlled at each stage at the moment of separation. It is often desirable to condense both forms A and B: this two-fold condensation procedure yields two final samples $A_f$ and $B_f$, enriched in different components. By comparing the degrees of separation of these two samples it is possible to double the accuracy of the determination of the separation coefficient.

The efficiency of the condensation process depends on two factors: the number of separation stages and the distribution of the degree of condensation over the stages. The degree of condensation of one stage is defined as the reciprocal of the recovery $\theta$, i.e. the ratio of the amount of the form to be extracted obtained at the stage $(j-1)$ to the amount of the same form obtained at the $j$th stage: $L_j = G_{j-1}/G_j$. Katal'nikov and Boreskov [17] studied this problem and showed that for a given number of stages $n$ and a given total degree of condensation ($L_\Sigma = \Pi_i L_i$) the maximum separation is obtained for equal degrees of condensation at all stages: $L_j = \sqrt[n]{L_\Sigma}$. They also showed that for a given degree of condensation the separation increases approximately exponentially with the number of stages: hence it is rational to choose a relatively small number of condensation stages (Fig. 2).

The same authors [17] proposed an accurate graphical method of calculation of small values of $\epsilon$ from the results of multistage extraction experiments for binary mixtures. This method is similar in many ways to the familiar

procedure for computing the number of theoretical plates. It enables the concentration of one of the components to be very simply computed after any number of extraction stages, whether one form is being extracted or both simultaneously. However, a knowledge of $\alpha$ is needed before the graphical method can be applied. The calculation is therefore made by trial and error, and the correlation between $\epsilon$ and $\Delta x_{\Sigma}$ is used to give a more accurate value of $\epsilon$.

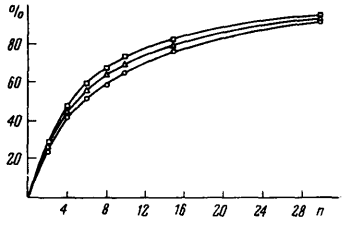



**Figure 2.** Ratio $\frac{\ln Q_{m.e.}}{\ln Q_{c.e.}}$, expressed as %, against number of condensation steps $n$. $Q_{m.e.}$ is the separation of the components of a binary mixture by the multistage extraction method, $Q_{c.e.}$ is the separation of the same mixture by Rayleigh's continuous extraction method. Circles for $\alpha = 1.001$; triangles for $\alpha = 1.010$; squares for $\alpha = 1.100$.

Kuznetsova and coworkers [18] proposed an analytical expression for calculating $\epsilon \ll 1$ directly from multistage extraction results ($n$ stages) assuming an equal degree of condensation for each stage:

$$\alpha = \frac{\sqrt[n]{\frac{x_0}{x_n}} - \theta}{1 - \theta}. \qquad (7)$$

This equation is not entirely satisfactory, because it can be applied only at low concentrations of one component. Outside the low concentration region the relative error in $\epsilon$ becomes large, since it is directly proportional to $x_0$.

The equation proposed by Mikhailichenko and Shcheglov [19] is free from the last two drawbacks, but it also applies only for $\epsilon \ll 1$:

$$\varepsilon = \frac{x_n - x_0}{x_0(1 - x_0)\left(n - \sum_{j=1}^{n} Q_j\right) - x_0(x_n - x_0)}. \qquad (8)$$

An analogous expression for an $n$-component mixture ($\epsilon_{ek} \ll 1$) was obtained by Knyazev and Bantysh [20]:

$$\varepsilon_{ek} = \frac{\ln Q_{ek}}{n - \sum_{j=1}^{n} \theta_j - \sum_{l=k}^{m} x_l}. \qquad (9)$$

Hence $\epsilon_{ek}$ is the enrichment coefficient, referred to some reference component $k$, $Q_{ek}$ and $Q_{jk}$ are the separations of components $j$ and $e$ with respect to the reference component. When the separation coefficients are significantly different from unity ($\epsilon \leqslant 0.2$) this expression becomes inaccurate. In these cases systems of equations of the following form must be used:

$$\ln Q_{ek} = \varepsilon_{ek} \sum_{j=2}^{m} \frac{1 - q_j}{1 + q_j \sum_{i=1}^{i} \varepsilon_{ik} y_{ij}} - \frac{\varepsilon_{ek}^2}{2} \sum_{j=2}^{m} \frac{(1 - q_j)^2}{\left(1 + q_j \sum_{i=1}^{n} \varepsilon_{ik} y_{ij}\right)^2}. \qquad (10)$$

The system can be solved by successive approximation; the first approximation for $\epsilon_{ek}$ can be the values given by Eqn. (9), and $\sum_{i=1}^{n} \epsilon_{ik} y_{ij}$ for each stage can be evaluated with sufficient accuracy by assuming that this sum is linear in the number of stages $j$. When the assumption that the quantity $\epsilon_{ek}$ is linearly related to some known parameter of the component $e$ can be justified, measurement of all the $Q_{ek}$ becomes superfluous, and only the separations of the two "extreme" (most easily separable) components needs to be measured. For example, in multicomponent isotopic mixtures $\epsilon_{ek}$ varies linearly with the isotopic mass $M_e$:

$$\varepsilon_e = \varepsilon_0 (M_e - M_k).$$

By using expressions of this type Eqn. (10) can be rewritten

$$\varepsilon_0 = \frac{\ln Q_{ek}}{(M_e - M_k)\left(m - 1 - \sum_{j=2}^{n} q_j\right) - \ln Q_{ek} \sum y_{i0} (M_e - M_k)}. \qquad (11)$$

The method has been most generally applied to measurements of the separation coefficients of isotopes. Many systems involving heterogeneous isotope exchange have been investigated, including solution–sorbent, solution–crystals, and liquid–liquid systems [21–26]. The main attraction of the method is that it can be applied without special equipment, using only the apparatus needed to measure $\epsilon$ by the single contact method.

## V. RAYLEIGH'S CONTINUOUS EXTRACTION METHOD

Rayleigh's method [27,28], also known as the continuous extraction or residue concentration method, is most commonly applied in distillation theory. It does not suffer from any of the limitations of the separation methods discussed above, and is undoubtedly applicable to the most diverse systems even though it is mostly used in studies of liquid–vapour equilibria at present.

The main difficulty associated with the Rayleigh method is the need to observe two sets of conditions at the same time: on the one hand, the concentrated (extracted) form must be free from concentration gradients, and on the other hand the concentration of this form and the take-off of the resulting new form must be carried out in infinitesimally small amounts. It is not difficult to comply with these conditions in simple distillation, but the study of other separation processes by this method is often complicated by the properties of the forms under investigation, or may require special experimental techniques.

The advantages of the method include: relatively high separation, allowing the separation coefficients to be measured accurately; non-equilibrium as well as equilibrium processes can be investigated; short experimental time (in the study of fast processes); relatively simple apparatus.

Since the method can be applied to a wide variety of separation processes, we shall describe it in the most general terms. Let the system have $n$ components, and assume that each component can exist in two states (1 and 2). At the beginning of the experiment the whole of the mixture ($G_0$) is in state 1. We assume that the mixture can be transferred by some method from state 1 to state 2 in infinitesimally small increments $dG$, and that a method for instantaneously removing the mixture in state 2 is available. We further assume that the transition of an

arbitrary component ($i$) from state 1 to state 2 occurs with probability $P_i x_i$, where $P_i$ is in general some function of the concentration of all the components in the mixture ($x_i$) in state 1, and also of the experimental conditions. Lastly, let the concentrations of the substances in the mixture in state 1 be described by their mole fractions $x_i$, and those in state 2 by their mole fractions $y_i$. It can easily be shown that the following relationship exists between the quantities $x_i$, $y_i$, $P_i$, $dG_i$, and $dG$:

$$\frac{dG_i}{dG} = y_i = P_i x_i = P_i \frac{G_i}{G}. \qquad (12)$$

Dividing Eqn. (12) for component $i$ by the analogous equation for component $j$, we obtain after some simple transformations

$$d \ln G_i = \frac{P_i}{P_j} d \ln G_j. \qquad (13)$$

The probability functions $P_i$ and $P_j$ depend on a number of factors, including first of all some specific properties of states 1 and 2. For example, we may be considering two processes as closely related as equilibrium distillation and vacuum distillation of liquid mixtures. In the former, the probabilities of $1 \rightarrow 2$ transitions will be determined by temperature and by the difference between the thermodynamic properties of the components in the different states; in the latter, they will be determined by temperature and by the molecular weight of the components. Furthermore, pressure, reactions with extraneous chemical compounds, concentration gradients, etc. may also affect the values of $P_i$ and $P_j$. Lastly, the dependence of $P_i$ and $P_j$ on the concentration of the components $i$ and $j$, and of other components undergoing the transition $1 \rightarrow 2$, should in general be considered. For a Rayleigh process in which all conditions except the concentrations of the $i$ and $j$ components are kept constant, integration of Eqn. (13) is possible only if the functions $P_i$ and $P_j$ are available in an explicit form. However, at least as regards thermodynamic separation processes, near-unity separation coefficients can be taken as evidence that the mixtures under study are close to ideality. This implies constancy of $P_i$ and $P_j$ (and even more so of their ratio $P_i/P_j$). Since the separation coefficient can be accurately measured with relatively small concentration changes, the assumption is fully justified. Thus, if the above assumptions hold true,

$$\frac{P_i}{P_j} = \frac{y_i}{x_i} \cdot \frac{x_j}{y_j} = \alpha_{ij} = \text{const}.$$

After integration we have

$$\ln \frac{G_{i_0}}{G_i} = \alpha_{ij} \ln \frac{G_{j_0}}{G_j}. \qquad (14)$$

Transformation of Eqn. (14) gives the following forms of the Rayleigh equation:

$$\ln Q_{ij} = \ln \frac{x_{i_0}}{x_i} \cdot \frac{x_j}{x_{j_0}} = \ln \frac{y_{i_0}}{y_i} \cdot \frac{y_j}{y_{j_0}} = \varepsilon_{ij} \ln \frac{G_{j_0}}{G_j}. \qquad (14a)$$

$$\ln Q_{ij} = \varepsilon_{ij} \left[ \ln \frac{G_0}{G} + \ln \frac{x_{j_0}}{x_j} \right] = \varepsilon_{ij} \left[ \ln \frac{G_0}{G} + \ln \frac{y_{j_0}}{y_j} \right]. \qquad (14b)$$

The approximate form

$$\ln Q_{ij} = \varepsilon_{ij} \ln \frac{G_0}{G}, \qquad (14c)$$

can be used if $\epsilon_{ij} \ll 1$.

For the case of two-component systems, Eqn. (14) can be converted into well known, precise expressions in which the ratio of concentrations of component 1 is presented[27] as a function of the degree of condensation[25]:

$$\ln \frac{x_{10}}{x_1} - \alpha \ln \frac{1 - x_{10}}{1 - x_1} = (\alpha - 1) \ln \frac{G_0}{G}.$$

$$Q = \frac{x_{10}}{x_1} \cdot \frac{1 - x_1}{1 - x_{10}} = \left( \frac{G_0}{G} \right)^{\alpha - 1} \left( \frac{1 - x_{10}}{1 - x_1} \right)^{\alpha - 1}. \qquad (15a)$$

For $\epsilon \ll 1$ we have

$$\ln \left( \frac{x_{10}}{1 - x_{10}} \cdot \frac{1 - x_1}{x_1} \right) = \ln Q \cong \varepsilon \ln \frac{G_0}{G}, \qquad (15b)$$

and with the additional condition $x_{10} \ll 1$, leading to $\alpha = y/x$, we obtain

$$\ln Q \ln \frac{x_{10}}{x_1} \approx \ln \frac{y_{10}}{y} \approx \varepsilon \ln \frac{G_0}{G}. \qquad (15c)$$

It is evident from Eqns. (14), (14a), and (15c) that measurement of $\alpha_{ij}$ requires only a knowledge of the initial and the final amount of material in the mixture in state 1 (to be condensed), as well as of the concentrations of the components of interest at those times. In other words, these quantities need to be known, in principle, before the beginning of the process and at any one time during the process. In this sense, Eqn. (14) and Eqns. (14a)–(14c) are equivalent. However, they are far from being equivalent as regards the accuracy with which ($\alpha_{ij} - 1$) can be calculated. As can readily be shown, the relative errors in the calculation of $\epsilon_{ij}$ by Eqn. (14) and by the widely used Eqn. (14c) are given, respectively, by the expressions

$$\frac{\Delta \varepsilon_{ij}}{\varepsilon_{ij}} = \frac{\Delta \ln Q_{ij}}{\ln Q_{ij}} + \frac{\Delta \ln z}{\ln z} \qquad (16a)$$

$$\frac{\Delta \varepsilon_{ij}}{\varepsilon_{ij}} = \frac{\Delta \ln Q_{ij} + 2 \Delta \ln z}{\ln Q_{ij}}. \qquad (16b)$$

Since $Q_{ij}$ is usually close to unity, the second term in the numerator of the right-hand side of Eqn. (16b) contributes very significantly to the overall error, whereas the second term in the right-hand side of Eqn. (16a) is small because of the magnitude of $\ln z$. Because $Q_{ij}$ does not differ much from unity and is therefore difficult to measure accurately, multiple measurements of $Q_{ij}$ and $z$ are desirable. Since samples of the "condensed" state 1 are usually more difficult to remove, and involve a correction for the effective degree of condensation $z$, it is preferable to analyse the material in the "drawn off" state 2. In the case of simple distillation, for example, vapour samples are usually analysed.

Any method of analysis requires a finite sample of the material to be analysed. It is important to establish the relationship between the size of the sample and the size of the permissible final residue of extracted mixture in state 1. It can be shown that the error arising from the discrepancy between the theoretical concentration (corresponding exactly to $G$) and the actual mean concentration becomes negligible if the degree of condensation is calculated for a value of $G$ corresponding to the "mean point" of the sample taken off (volume $2\Delta G$). When the degree of condensation is calculated in this way, the relative error in the measurement of concentration becomes

$$\frac{\Delta y}{y} \cong -\frac{(\alpha - 1)}{3} \left( \frac{\Delta G}{G} \right)^3. \qquad (17)$$

Thus, the removal of samples of finite volume does not impose rigid limitations on the size of the minimum permissible final residue. This allows significant degrees of condensation to be achieved without serious error.

Until recently, Rayleigh's method has been applied to the measurement of small separation coefficients when the

process under investigation is not complicated by the presence of extraneous separation processes, and when the experimental arrangements needed to realise the basic conditions of the Rayleigh process are not unduly complex. These requirements are easily met in simple distillation processes, and in particular in the equilibrium distillation of mixtures consisting of members of a series of related compounds or other materials with closely similar properties [29], in the molecular distillation of isotopic mixtures [30], in some isotope exchange processes [31], in electrolytic methods of isotope separation [32,33], and also in separation processes relying on equilibrium crystallisation from aqueous solutions [34].

More recently, Rayleigh's method has been shown to be applicable to the study of homogeneous isotope exchange and exchange in heterogeneous extraction, ion-exchange, and other heterogeneous systems [35-37].

Lastly, the Rayleigh process can be used to study separation phenomena such as the diffusion of gases through porous partitions, diffusion through liquid films, etc.

## 1. Rayleigh Distillation

Rayleigh's method is used mostly to study separation in liquid–vapour systems, for which the correct experimental conditions have been most accurately identified and suitable apparatus and experimental procedures have been developed. Only the basic features of the method will be discussed in the present review: some of these are general features, others are more specific. Even the latter, however, are almost invariably present (in a modified form) in other separation processes as well.

In the experimental realisation of Rayleigh's method, various specific features of the distillation process itself must be taken into account. Furthermore, the simpler laboratory assemblies invariably present some undesirable aspects which must be minimised. Lastly, some unavoidable phenomena must quantitatively evaluated and allowed for.

1. True liquid–vapour equilibrium occurs when the evaporation and condensation fluxes are equal. Since evaporation of the liquid must proceed at a practically useful rate in the Rayleigh process, this process is a quasi-stationary one, and the separation coefficients obtained can approach the equilibrium values only in the most favourable (or most unfavourable) cases [38,39]. Obviously, the measured coefficients will be closer to the equilibrium values, the smaller the vapour take-off is in relation to the exchange flow of material between liquid and vapour. In practice, the optimum rate of evaporation is found experimentally, by monitoring the dependence of the observed separation coefficient ($\alpha$) on the evaporation rate. The range of evaporation rates corresponding to a constant value of $\alpha$ is chosen for the experiment. Conversely, in molecular distillation the true value of the separation coefficient can only be obtained in the total absence of vapour condensation. This condition can be met by removing the evaporated material from the vicinity of the liquid as rapidly as possible [30].

2. The application of the integral forms of the Rayleigh equation presupposes constancy of the separation coefficients. As stated above (see p. 571), this in turn implies independence of the separation coefficient upon the composition of the mixture and constancy of temperature. In practice, the process is most frequently applied at constant pressure [29]. As the composition of the liquid phase changes, the boiling point under isobaric conditions also changes. However, near-unity separation coefficients usually imply that the substances to be separated have similar boiling points, so that at moderate degrees of separation isobaric evaporation is a good approximation to isothermal evaporation. This is also true when the components differ significantly in boiling point provided that the measurements are confined to low concentrations of one component. In these cases, the condition of constancy of the separation coefficient is automatically satisfied.

3. It follows from the initial, differential form of the Rayleigh equation (Eqn. (12)) that the composition of the sample must be representative of that of the whole of the condensed phase. From the standpoint of equilibrium and molecular distillation, this implies that the composition of the liquid near the evaporating surface must be identical to the composition at any other point in the liquid phase, i.e. that the liquid phase must be free from concentration gradients. Mechanical stirring is therefore widely used. The stirring conditions depend on the design and type of stirrer, and are chosen empirically. The criterion for satisfactory stirring is independence of the observed value of $\alpha$ upon the intensity of stirring (number of revolutions per minute).

4. The definition of separation coefficient in both equilibrium and molecular distillation implies that the vapour phase must be strictly homogeneous and must not contain any particles of the liquid phase. Since boiling of the bulk liquid usually gives rise to a large amount of spray, the distillation process is usually carried out under conditions approximating to isothermal evaporation from the surface, which imposes severe limitations on the effectiveness of mixing. Stirring helps to avoid overheating of the liquid and to obtain quiet evaporation. However, the intensity of stirring must be kept below the limit at which spray formation sets in.

5. The equilibrium separation coefficient in distillation cannot be measured under conditions leading to multiple separation acts. Hence, vapour condensation and reflux from the vapour to the liquid is permissible only at the main condensation surface. Vapour condensation in the vapour volume and at the walls of the evaporation vessel must be excluded, and hence the vapour and the walls of the evaporator must be kept at a temperature such that condensation is impossible.

6. Evaporation vessels are usually designed (Fig. 3) so that the total volume occupied by the liquid and the vapour phase is constant throughout the experiment. Under these conditions the amount of material in the vapour state at the end of the experiment is comparable with the amount of liquid mixture. Mechanical stirring of the liquid may be supplemented by stirring of the vapour, which is even more effective, since it brings a finite amount of the vapour phase into equilibrium with the liquid rather than an infinitesimally thin layer. Allowing for these conditions [39], the initial differential and the final integral equation for the process should be written in a form which differs substantially from Eqn. (12) and following. Allowing for the volume of the stirred vapour phase leads to the equations:

$$\lg\frac{y_i}{y_f}=\lg\frac{x_i}{x_f}=\frac{\alpha\,(v_v-v_l)}{v_v-\alpha v_l}\cdot\lg\frac{G_i\,(v_v-\alpha v_l)+\varepsilon V}{G_f\,(v_v-\alpha v_l)+\varepsilon V}+\lg\frac{G_f}{G_i} \qquad (18a)$$

$$\lg\frac{x_i}{z_f}=\frac{\alpha\,(v_v-v_l)}{v_v-\alpha v_l}\cdot\lg\frac{G_i\,(v_v-\alpha v_l)+\varepsilon V}{G_f\,(v_v-\alpha v_l)+\varepsilon V}-\lg\frac{G_f\,(v_v-\alpha v_l)+\varepsilon V}{G_f\,(v_v-v_l)}+\lg\frac{G_f}{G_i} \qquad (18b)$$

$$\lg\frac{x_i}{x_f}=\frac{\alpha\,(v_v-v_l)}{v_v-\alpha v_l}\lg\frac{\alpha V+g_{li}\,(v_v-\alpha v_l)}{\alpha V+g_{lf}\,(v_v-\alpha v_l)}+\lg\frac{V+g_{lv}\,(v_v-v_l)}{V+g_{lf}\,(v_v-v_l)}. \qquad (18c)$$

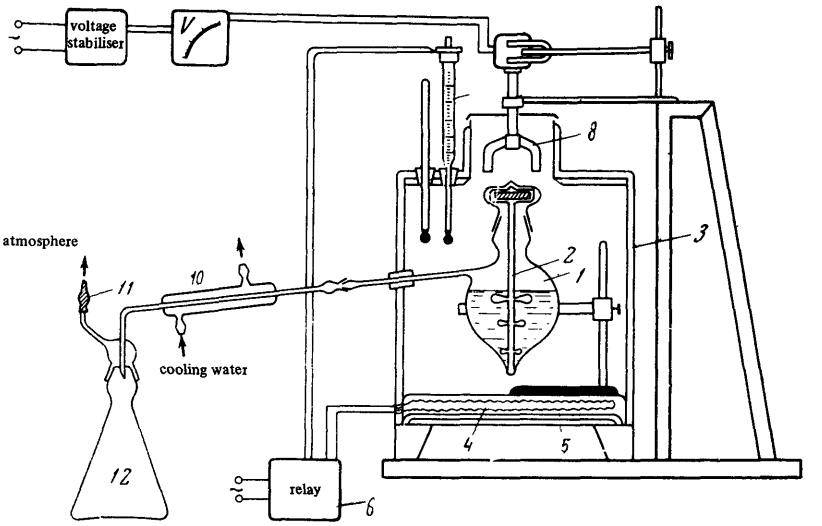



**Figure 3.** Apparatus for Rayleigh distillation; *1*) still; *2*) magnetic stirrer; *3*) air thermostat; *4*, *5*) electric heaters; *6*) relay; *7*) contact thermometer; *8*) magnet; *9*) voltage stabiliser; *10*) condenser; *11*) calcium chloride tube; *12*) receiver.

Here, $V$ is the volume of the Rayleigh still, $v_l$ is the molar volume of the liquid phase, $v_V$ is the molar volume of the vapour phase, $G$ is the number of moles of the mixture in the still, $x$ and $y$ are the mole fractions of the minority component in the liquid and the vapour phase respectively, $z$ is the mean concentration of the minority component in $G$ moles of mixture in the still; $x, y \ll 1$, $\alpha = y/x$, $\epsilon = \alpha - 1$.

As Fig. 4 shows, using the Rayleigh equation directly in the form (14a)–(14c) and (15a)–(15c) leads to large errors in the measurement of $\alpha$, particularly at high degrees of condensation. If the separation is determined from an analysis of the vapour phase, and the degree of condensation is measured as the ratio $G_0/G_i$, the error is minimised, but even in this case degrees of condensation in excess of $10^2$–$10^3$ lead to intolerably high errors in $\alpha$.

7. Because of the need for visual observation of the progress of distillation and for an approximate estimate of the degree of condensation, evaporation stills are usually made of glass, which is not a good conductor of heat. This, in turn, produces significant temperature gradients at the walls of the still, and hence a temperature difference between the thermostat medium (air, or water) and the evaporation temperature must be specially maintained.

8. In addition to the designs involving mechanical stirring of the two phases, designs similar to the contact apparatus with rotating drums [7] and with inert carrier gas bubbling [31] have been proposed. These offer the advantage of a more precise temperature control of the contents of the still. In complicated systems, containing volatile impurities (see p. 574), this facility is extremely valuable, because the boiling point of these mixtures at constant pressure is a sensitive function of composition. Furthermore, the process takes place much faster, with a consequent reduction in the duration of the experiment. These designs can be additionally provided with facilities for liquid circulation, resulting in a large increase in the initial volume of liquid and hence in an enhanced ultimate degree of condensation and of separation. Lastly, these advanced designs allow the volume of vapour in equilibrium with the liquid to be kept small and constant, which largely removes the limitations discussed above and simplifies the experimental procedure.

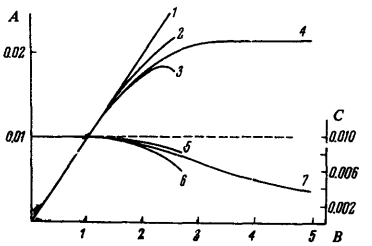



**Figure 4.** Plots of separation ($x_i/x_f$, $x_i/z_f$) against degree of condensation ($G_i/G_f$, $g_i/g_f$) assuming complete mixing of the vapour phase. Plots of the effective enrichment coefficient $\epsilon$ against degree of condensation assuming complete mixing of the vapour phase. *A*) values of $\lg\frac{x_i}{x_f}$ and $\lg\frac{x_i}{z_f}$; *B*) values of $\lg\frac{g_i}{g_f}$ and $\lg\frac{G_n}{G_f}$; *C*) effective $\epsilon$ values. Condensation conditions: initial amount of mixture $G_i = 10$ mole, volume of Rayleigh still $V = 0.6$ litre, molar volumes of liquid ($v_l$) and vapour ($v_V$) 0.05 and 22.4 litre mole$^{-1}$ respectively, equilibrium value of the enrichment coefficient $\epsilon = 0.010$. Curves *1*, *2*, *3*, and *4* correspond to Eqns. (14a), (18a), and (18c) respectively. Effective $\epsilon$ values calculated from Eqn. (14a), allowing for the actual degrees of separation and condensation by means of Eqns. (18a)–(18b); curves *5*, *6*, and *7* correspond to Eqns. (18a), (18b), and (18c) respectively.

2. Rayleigh's Equation in a Form Suitable for Studying the Dependence of $\alpha$ on the Composition of the Phases

The integral forms of Rayleigh's equation given above were obtained on the assumption of constant separation coefficients $\alpha_{ik}$. This condition is often inappropriate, and the equations given above then lead to some average value of $\alpha_{ik}$. There is a simple method by which true values of $\alpha_{ik}$ can be obtained, and related to any concentration of the component $k$ which is encountered during Rayleigh extraction [40,41]. A different mathematical procedure is used, based on a more convenient form [13] of the differential Rayleigh equation:

$$d\ln Q_{ik} = -\varepsilon_{ik}(d\ln G + d\ln x_k), \qquad (19)$$

whence

$$\varepsilon_{ik} = \frac{\dfrac{d\ln Q_{ik}}{d\ln G}}{1+\dfrac{d\ln x_k}{d\ln G}}. \qquad (20)$$

Since $Q_{ik}$ varies as a function of $G$ during the extraction, the wanted differentials are readily found from the analytical results obtained by any convenient method. The most accurate results are obtained by expressing $\ln Q_{ik}$ and $\ln x_k$ (or $\ln x_k$ and $\ln x_i$) in the form of Lagrange polynomials, which can then be differentiated numerically. Graphical differentiation procedures are also possible (from experimental plots of $x$ against $\ln G$).

In the case of two-component mixtures the problem becomes simpler, since $x_2 = 1 - x_1$, and the relationship between $\ln x_1$ and $\ln G$ is sufficient to define $\alpha$. For $\epsilon \ll 1$ (and particularly for $x_k \ll 1$) the differentials $\dfrac{d\ln x_k}{d\ln G}$ become negligibly small, and the expression takes the form

$$\varepsilon_{ik} = \frac{d\ln Q_{ik}}{d\ln G} = \frac{d\lg Q_{ik}}{d\lg G}. \qquad (21)$$

Examples of the use of these expressions can be found in the literature [29,40]. The experimental technique differs from the Rayleigh distillation procedure (see p. 577) in that the amount and composition of the distillate are monitored periodically. From these measurements it is a simple matter to calculate the amount and composition of the liquid in the still and to establish the dependence of $\lg Q$ upon $\lg G$. For the case of $\alpha$ = const this dependence will take the form, according to Eqn. (21), of a straight line of slope $\alpha$.

3. Application of the Rayleigh Equation to Measurements of Separation Coefficients in the Presence of Additives, During Extraction, and During Ion Exchange

Additives showing preferential chemical or physical interaction with one or several of the components of a mixture, and therefore having a beneficial effect on the separation coefficient, have been used increasingly in recent years to facilitate the separation of difficult mixtures. Additives in various forms have been used in practically all countercurrent processes, in which separation depends on phase equilibria or chemical equilibria (azeotropic and extractive distillation, extraction and ion exchange at low degrees of complex formation in the aqueous phase).

The effective separation coefficient in the presence of additives is determined by two effects: the phase equilibrium, and the physical or chemical equilibrium between the initial forms of the components and the additive. The interaction can take place in one of the phases under study, or in both phases. In either case the Rayleigh process is complicated by the fact that the concentration of the additive (and therefore also $\alpha$) varies as the condensed phase is removed. Nevertheless, useful analytical expressions for the separation coefficient relevant to the homogeneous exchange process can be obtained by making some specific assumptions as to the nature of the homogeneous exchange of the components between their initial form and their reaction products with the additive. This approach can be used to evaluate the effectiveness of the additive and to study the homogeneous reactions involving the additive.

**Table 2.**

| Method | Logarithm of enrichment in the liquid phase as a function of degree of condensation. Isothermal regime | Logarithm of enrichment in the vapour phase as a function of degree of condensation. Isothermal regime |
|---|---|---|
| With involatile additive | $\ln\frac{z}{z_0} = \frac{1}{\alpha}\ln\frac{G_c+\beta G_a^0}{G_c+\beta G_a} - \ln\frac{G_c+G_a}{G_c+G_a^0}$ | $\ln\frac{x}{x_0} = \frac{\alpha-1}{\alpha}\ln\frac{G_c+\beta G_a^0}{G_c+\beta G_a}$ |
| With volatile additive | $\ln\frac{y}{y_0} = \frac{\gamma-\alpha}{\alpha(\gamma-1)}\ln\frac{\beta-c(\beta-1)}{\beta-c_0(\beta-1)} + \frac{(\alpha-1)\gamma}{\alpha(\gamma-1)}\ln\frac{c}{c_0}$ | $\ln\frac{x}{x_0} = \frac{(\alpha-1)}{\alpha(\gamma-1)}\ln\frac{[\beta+(\gamma-\beta)\bar{c}]\bar{c}_0}{[\beta+(\gamma-\beta)\bar{c}_0]\bar{c}} + \ln\frac{\beta+(\alpha-\beta)\bar{c}}{\beta+(\alpha-\beta)\bar{c}_0}$ |
| Extraction | $\ln\frac{Z_f}{Z_0} = \ln\frac{x_f}{x_0} = (\alpha-1)\frac{\delta R}{\alpha\delta R+S}\ln\frac{G_0}{G_f}$ | |
| Ion exchange | $\ln\frac{x_f}{x_0} = \ln\frac{y_f}{y_0} = \frac{(\alpha-1)}{\alpha\delta R+S}\left[\delta R\ln\frac{G_S^f}{G_S^0} - \frac{S}{\alpha}\ln\frac{S+\alpha\delta R+(\delta-1)G_S^f}{S+\alpha\delta R+(\delta-1)G_S^0} - \left(\delta R-\frac{S}{\alpha}\right)\ln\frac{S+(\delta-1)G_S^f}{S+(\delta-1)G_S^0}\right]$ | |

$G_S$, $G_R$ are the amounts of mixture in the system in the organic and the aqueous layer respectively;

$R$, $S$ are the volumes of the organic and the aqueous phase in the case of extraction;

$R$, $S$ are the molar capacities of the organic and the aqueous phase in the case of ion exchange.

The simplest case is found when the additive is present in the phase to be extracted and cannot be transferred to the phase to be removed [35]. Such a process is characterised by the phase separation coefficient $\alpha$ and also by a separation coefficient $\beta$ which relates to the homogeneous reaction in the phase to be extracted. Then, from the differential form of the Rayleigh equation, we obtain

$$\frac{dz}{z-x} = \frac{dG}{G},$$

where $z$ is the mean concentration of the given component, $G$ is the amount of mixture in the phase to be extracted, and $x$ is the concentration of the same component in the phase to be removed. Starting from the differential form of the Rayleigh equation we can arrive at a number of expressions for isothermal conditions: these are set out in Table 2. They all involve the assumption that the phase and the homogeneous exchange equilibria are maintained at all times. Very low concentrations of the particular component are also assumed ($x$, $z \ll 1$).

The case of an additive which can distribute itself between the two phases is more complicated [36]. On the

assumption that equilibrium in the phase to be removed is determined by the same coefficient ($\beta$) as in the phase to be extracted, and that the distribution of the additive between the two phases can be described in terms of a distribution coefficient $\gamma$, the integral forms of Table 2 can be obtained from the differential form. Analogous expressions can be derived for the isobaric regime, but these are complicated by the need to allow for the temperature dependence of $\alpha$.[35]

In the above discussion of non-distributed and of distributed additives, the volume of phase to be removed (in equilibrium with the phase to be extracted) is assumed to be negligibly small. This condition is easily satisfied in Rayleigh distillation, but not in extraction or in ion exchange processes. In the latter, the condition of constant volume of the two contacting phases is more easily realised. Hence, and using the distribution coefficient $\delta$ to characterise the phase equilibrium of the mixture as a whole for extraction systems and $\delta'$ for ion exchange systems, appropriate integral forms of the Rayleigh equations can be obtained[37]. These, too, are given in Table 2.

The tabulated relationships are transcendental in $\alpha$ and $\beta$ (with the exception of the extraction equation). Hence, the required values must be found by selection or by successive approximation methods, which are in general very time-consuming.

## VI. SQUARE CASCADE METHODS

The term square cascades is used[42] in the general theory of separation processes to denote columns operating in the countercurrent regime and characterised by a constant flow of material at any cross-section. We shall retain this term in order to include in the following discussion, without distinction of any kind, processes such as rectification, extraction, hypersorption, development chromatography, heterogeneous isotope exchange, and others. Cascade methods enable the separation effects under study to be strongly enhanced, leading to reliable and accurate measurements of $\alpha$ and $\epsilon$. It is usually necessary to resort to these methods when $\epsilon$ is small, particularly if the apparatus is simple and no preliminary investigation of the process is required (rectification, development chromatography).

The separation obtainable in square cascades is characterised by the number of theoretical plates ($n$), which is a function of the hydrodynamic operating regime of the cascade, and of the properties of the mixture to be separated. Thus, the determination of $\alpha$ by a cascade method is always a problem with two unknowns, requiring two independent equations. Bearing in mind that the measurement error associated with various characteristics of the process can seriously degrade the accuracy of the measurement of $\alpha$ and $n$, it is often the best practice to extract these values from the largest possible number of experiments over the widest possible range of cascade parameters.

### 1. Equations for Stationary Operating Regimes of the Cascade

States of the cascade for which all parameters and their characteristics remain constant with time are termed stationary states.

We shall deal first with the equations and methods which apply to total reflux conditions. The separation $Q_{ie}$ is related to the separation coefficient $\alpha_{ie}$ of a cascade with $n$ theoretical stages by the Fenske-Underwood equation[43,44]

$$Q_{ie} = \alpha_{ie}^{n}. \qquad (22)$$

In order to calculate $\alpha_{ie}$ from the experimentally observed value of $Q_{ie}$ we must know the number $n$ of theoretical separation stages under the conditions of the particular experiment. In the case of two-component mixtures, we can use the mass conservation equation for one of the components for this purpose, and arrive[45] at the following analytical expression for $\alpha$:

$$\ln \alpha = \frac{G \int_{h_1}^{h_2} (x - x_0)\, dn}{G \cdot \ln \frac{1 - x_{h_2}}{1 - x_{h_1}}}.$$

In this expression the numerator is the experimentally measurable excess of the component under study in a section of the cascade between points $h_1$ and $h_2$ (as compared with the initial state, for which the concentration is everywhere $x_0$). $G$ is the number of moles of material in the same section of the cascade, $x_{h_1}$ and $x_{h_2}$ are the concentrations of the component at the points $h_1$ and $h_2$.

In practice, measurements of $\alpha$ have often been made by inserting into the Fenske–Underwood equation the number of theoretical plates, obtained by independent methods. The precision of the measurement of $\alpha$ by Fenske–Underwood equation is much more sensitive to errors in $n$ than to errors in $Q_{ie}$:

$$\frac{\Delta \ln \alpha_{ie}}{\ln \alpha_{ie}} = |\Delta \ln \ln Q_{ie}| + |\Delta \ln n|. \qquad (23)$$

For the case of rectification in unpacked, liquid-film columns the number of plates $n$ can be calculated to an accuracy of 10–15% from the parameters of the column and from the flow by using semi-empirical relations[46,47]. This calculation cannot yet be made in the case of the more efficient, packed columns, and an approximate estimate of $\alpha$ for these columns is sometimes made by inserting the value of $n$ obtained for a model mixture (with physicochemical properties as close as possible to those of the unknown mixture) in the same cascade[45]. Bushmakin and coworkers[48–50] suggested the measurement of $\alpha$ at low concentrations of one of the components by using the number of theoretical plates ($n$) obtained in experiments with the same mixture but at concentrations high enough to allow $\alpha$ to be measured by other methods. This procedure ignores the dependence of the HETP (height of the equivalent theoretical plate) upon composition, and must therefore be treated as approximate.

More accurate values of $\alpha$ are obtained if the separation $Q$ and the number of plates $n$ can be measured in a single experiment. This condition can be realised if the unknown mixture contains more than two components, and the separation coefficient $\alpha_{ik}$ for one pair of components is known. In this case there is a simple relationship which allows the unknown separation coefficients to be evaluated in terms of the known value $\alpha_{ik}$:[51,52]

$$\ln \alpha_{em} = \ln \alpha_{ik} \frac{\ln Q_{em}}{\ln Q_{ik}}. \qquad (24)$$

The equations for stationary separation regimes of multicomponent mixtures with take-off are complicated, and cannot be applied to the measurement of $\alpha$. The numerous and simpler relationships which have been proposed for binary mixtures[53–59], on the other hand, can be used. Experimental tests of some of these equations have been carried out[60–62]. The procedure for measuring $\alpha$ in

the presence of take-off involves measuring the separation of the mixture by the cascade either as a function of relative take-off or as a function of the position of the take-off point (multipoint take-off). In both cases a large number of experiments is desirable, followed by statistical treatment of the results, because the separation is very sensitive to the take-off ratio, which cannot be measured with great precision. Since the equations for the take-off regime are transcendental in $\alpha$, it is convenient to use the so-called graphical least-squares method, which does not require normal equations to be set up[63,64]. Smoker's equation, which applies for any value of $\alpha$ and any concentration of either component, is presented in Table 3.

**Table 3.** Operating equation of the column in the stationary regime:

$$\left(\frac{\alpha}{\gamma c^2}\right)^n = \frac{x'}{x}\left[\frac{1-\left(\frac{\gamma c(\alpha-1)}{\alpha-\gamma c^2}\right)x}{1-\left(\frac{\gamma c(\alpha-1)}{\alpha-\gamma c^2}\right)x'}\right]. \qquad (25)$$

| Variable | Section of cascade | |
|---|---|---|
| | Rectifying | Scrubbing |
| $x'$ | $x_p-\beta$ | $x_0-\beta$ |
| $x$ | $x_0-\beta$ | $x_p-\beta$ |
| $c$ | $1+(\alpha-1)\beta$ | |
| $\beta$ root of equation $(0\leq\bar{x}\leq 1)$ $0<\beta<1$ | $\gamma(\alpha-1)\bar{x}^2+[\gamma+b(\alpha-1)-\alpha]\bar{x}+b=0$ | |
| $b$ | $x_p\Theta$ | $-\frac{x_p\Theta}{1-\Theta}$ |
| $\gamma$ | $1-\Theta$ | $\frac{1}{1-\Theta}$ |

$\gamma$ is the ratio of heavy phase and light phase flows; $\Theta$ is the relative take—off (product/feed); $x$ is the reduced concentration in the heavy phase; subscripts 0 and $p$ refer to the feed and the outlet section respectively.

Simpler equations, shown in Table 4, are used for the low-concentration region, when the equilibrium equation is linear[45,65-67].

## 2. Expressions for Non-stationary Regimes

During the establishment of a stationary state at any point in the cascade, the concentrations of the components show a continuous change which is (to a first approximation) exponential. In principle, the separation coefficient of a binary mixture can be calculated from measurements of the concentration of one of the components as a function of time. However, none of the many expressions which have been proposed to describe the achievement of steady state is truly exact[45,65,67-75]. This is because of the lack of accurate methods of solution of non-linear partial differential equations, such as the basic non-stationary state equation. The equations which have been proposed involve various simplifying assumptions on the distribution of concentrations along the column and with time; these assumptions do not usually lend themselves to strict mathematical analysis, and existing experimental data are insufficient for a detailed study of the assumptions.

The adequacy of the equations for non-stationary processes is most satisfactorily established by comparing the numerical values of various parameters given by the equations with the values obtained by numerical solution of the original differential equation on an electronic computer. Jackson and Pigford (quoted in Ref. 72) were able to show in this way that some published equations[68,70,71] were unacceptable. Other equations[72,74] were shown to be inaccurate by comparison with experimental results[45,67].

**Table 4.** Operating equations of the column in the stationary regime for the case $x \ll 1$.

| Section | Component | |
|---|---|---|
| | light | heavy |
| Rectifying | $Q=\frac{x_p}{y_0}=\frac{(\alpha-\gamma)\left(\frac{\alpha}{\gamma}\right)^n}{\gamma(\alpha-1)+\alpha(1-\gamma)\left(\frac{\alpha}{\gamma}\right)^n}$ | $Q=\frac{y_0}{x_p}=\frac{\gamma(\alpha-1)(\alpha\gamma)^n-(1-\gamma)}{(\alpha\gamma-1)}$ |
| Scrubbing | $Q=\frac{x_0}{x_p}=\frac{\left(\frac{\alpha}{\gamma}\right)^n(\alpha-1)-(\gamma-1)}{(\alpha-\gamma)}$ | $Q=\frac{x_p}{x_0}=\frac{(\alpha\gamma)^n(\alpha\gamma-1)}{(\alpha-1)+\alpha(\gamma-1)(\alpha\gamma)^n}$ |

$\gamma$ is the ratio of heavy phase and light phase flows; $n$ is the number of theoretical plates; $x$ is the concentration in the heavy phase; $y$ is the concentration in the light phase; subscripts 0 and $p$ refer to the feed and the outlet ends of the section respectively.

The equation of Babkov and Zhavoronkov[75] was tested most stringently against experiment and against a model of the achievement of steady state (electronic computer), and the discrepancy during the relaxation time was found to be insignificant (0.6%). Rozen's equation[67] also gave satisfactory results. The full forms of these equations are shown in Table 5 together with approximate expressions applicable at low concentrations. All these equations are transcendental in $\alpha$ and $Q_\infty$ (degree of separation at steady state). The usual procedure for calculating $\alpha$ is to insert the rather inaccurate experimental values of $Q_\infty$ into the kinetic equations. An additional source of error could be the inaccuracy of the kinetic equations themselves at times long compared with the relaxation time. The most satisfactory procedure is to calculate $\alpha$ and $Q_\infty$ together by least squares[63].

The mass conservation equation for either of the components to be separated can be used as an additional source of information on the value of $\alpha$. When high-efficiency cascade processes are used, the kinetic curves show an extensive linear portion, indicating that during an appreciable time the longitudinal transfer of any component is practically constant and is determined by the difference in equilibrium concentrations at the feed plate of the cascade. If the cascade flows ($L$) are constant, measurement of the amount of component $i$ accumulating in the cascade in time $t$ ($G\int_0^n (x_i - x_{i_0})dn$) enables this difference to be determined.

$$y_i^0 - x_i^0 = \frac{G\int_0^a (x_i - x_i^0)\,dn}{tL} \qquad (26)$$

The equations relating this difference to $\alpha_i$ can then be used to evaluate the latter.

Unlike the kinetic methods described above, the mass balance method offers two important advantages: on the linear portion of the kinetic curve, Eqn. (26) is both accurate and applicable to multicomponent systems. Of course, with multicomponent systems it becomes necessary to measure the integrated transport of all the components, whether or not the experimenter is interested in their separation. The accuracy of measurements of $\epsilon$ by this method is well illustrated by the excellent agreement with results obtained by other methods [67,76].

Table 5.

| Region of application | Analytical expressions for the time to reach steady state | Literature references |
|---|---|---|
| $0<x\leqslant 1$ | $t=\frac{1}{L}\left\{\frac{\varepsilon}{1+x_0\varepsilon}+\frac{\alpha}{\varepsilon(1-x_0)(1+x_0\varepsilon)^2}\left[(\alpha^n-1)\frac{1-x_n}{x_n-x_0}+\varepsilon\right]\ln\left(1+\right.\right.$ $\left.\left.+\frac{1+x_0\varepsilon}{x_0(\alpha^n-1)\frac{1-x_n}{x_n-x_0}}\right)\right\}\times\left[(x_n-x_0)\left(v_0-\frac{Hn}{\frac{1-x_n}{1-x_0}\alpha^n-1}\right)+\right.$ $\left.+\frac{H(\alpha^n-1)}{\ln\alpha}\cdot\frac{\frac{1-x_n}{1-x_n\alpha^n-1}}{1-x_0}\cdot\ln\frac{1-x_0}{1-x_n}\right]$ | 75 |
| $x\ll 1$ | $t=\frac{1}{L}\cdot\frac{\alpha}{\alpha-1}\left[\left(H\frac{\alpha}{\alpha-1}+v_0\right)\cdot(\alpha^n-1)-nH\right]\cdot\ln\frac{\alpha^n-1}{\alpha^n-\frac{x_n}{x_0}}$ | 75 |
| $0<x\leqslant 1$ | $M=\left\{v_0\frac{(\alpha^n-1)(1-x_0)}{1+x_0(\alpha^n-1)}+H\left[\frac{\ln[1+x_0(\alpha^n-1)]}{x_0\cdot n\cdot\ln\alpha}-1\right]\right\}x_0;\ t_0=\frac{M}{j_0}$ | 67 |
| $x\ll 1$ | $t_0=\frac{\left[v_0(1-e^{\varepsilon.i})+H\left(1-\frac{1-e^{\varepsilon.i}}{\varepsilon n}\right)\right]}{L\varepsilon}$ | 67 |

$t$ is the time to reach steady state, $L$ is the flow of material in the column (mole $h^{-1}$), $x_0$ and $x_n$ are the initial and the final concentration, $n$ is the number of theoretical plates, $H$ is the delay for one plate, $v_0$ is the capacity of the still, $t_0$ is the total relaxation time of the column, $j_0$ is the limiting transfer, $M$ is the total equilibrium hold-up in the column.

## VII. CHROMATOGRAPHIC METHODS

The field of application of chromatographic methods of measuring separation coefficients is rapidly expanding. It already includes phenomena such as liquid–vapour and liquid–gas equilibria, sorption of vapours and gases on solid sorbents, ion exchange and non-ionic sorption on resins, liquid–liquid equilibria, and homogeneous reactions in solutions. These methods are being applied to the separation of a wide variety of mixtures. Examples of their successful application to the separation of every kind of difficult mixture can be found in numerous textbooks, review articles, and bibliographies. We need only mention some of the most important classes of mixtures: isotopes, isomers, inorganic and organic polymers, rare earths and actinides, numerous homologues and genetically related compounds, aminoacids, polypeptides, sugars, and other biologically active materials.

All three main variants of the chromatographic process (elution, frontal, and displacement methods) can be used to measure small separation coefficients. The development or elution method has attracted most attention, the frontal method has attracted the least. A vast amount of work has been devoted to the separation of the most diverse materials by elution, but often the authors have neglected to calculate the separation coefficients even when sufficient information was available.

We shall consider below the special equations which allow measurement of $\epsilon$ from quite small separation effects in small columns. These equations are valuable mainly in measurements of $\epsilon \ll 1$, i.e. in problems as difficult as isotope separation, but they can also be used successfully in the study of many other difficult mixtures.

### 1. Elution Chromatography

The principle of the method is the following: a sample of the mixture to be separated, containing much less material than the total capacity of the sorbent in the column, is introduced at the top of the chromatographic column. A mobile phase (liquid or gas) containing a displacement agent is then used to elute the sample. The condition for the establishment of the elution regime is that the affinity of the displacement agent for the sorbent must be less than the affinity of any component of the mixture. As a result of elution, the components move downwards along the column, at different rates, and gradually become separated. In addition, each individual band becomes broader as it moves downwards. The effluent at the bottom of the column consists of concentration waves of the various components, overlapping to a greater or lesser extent. The extent of overlap depends on the distribution coefficients of the components between the mobile and the stationary phase, and also on the length and the efficiency of the packing, and on the operating regime of the column. Initially, the form of the concentration peaks depends on the type of the adsorption isotherms of the components, but further down the column it approaches the shape of a Gaussian distribution. If the adsorption isotherms are linear and mutually independent, the relationship between the distribution coefficients $\lambda_i$ of the components, their separation coefficients $\alpha_i$, and the volumes $v_i$ and $v_j$ of the mobile phase for which the respective concentrations are at a maximum takes the simple form

$$\alpha_{ij}=\frac{\lambda_i}{\lambda_j}=\frac{\bar{v}_i-v_0}{\bar{v}_j-v_0};\quad \varepsilon_{ij}=\frac{\bar{v}_i-\bar{v}_j}{v_j-v_0}, \tag{27}$$

where $v_0$ is the free volume of the column.

Thus, the measurement of separation coefficients by elution chromatography involves, firstly, the establishment of conditions consistent with the assumptions made in the derivation of the equations, and secondly a very accurate measurement of the quantities $\bar{v}_i$, $\bar{v}_j$, and $v_0$.

The condition of linearity and mutual independence of the sorption isotherms is best satisfied at low concentrations of the materials to be separated. However, the initial concentration of the mixture in the mobile phase is usually fairly large, and in relatively short columns the concentration peaks do not achieve the Gaussian form. In long columns, the concentration peaks travel through most of the distance at fairly low concentrations, such that the sorption–desorption process takes place in the linear part of the isotherm. Also, the components in this case are almost completely separated provided that the enrichment coefficient $\epsilon$ is not too small, and the problem of possible interaction between the components ceases to be relevant. If the separation achieved is sufficient to allow direct measurement of $\bar{v}_i$ and $\bar{v}_j$, the separation coefficient is measured directly by means of Eqn. (27).

When the isotherms show substantial deviation from linearity, the concentration peaks are often seriously distorted when separation is complete. In these cases formula (27) gives only approximate values of $\epsilon_{ij}$, and a better estimate is obtained by inserting $\bar{v}_i$ values corresponding to the centre of gravity of the various bands [77] instead of the concentration maxima.

When $\epsilon_{ij} \ll 1$, and also when short columns are used, the individual bands overlap so strongly that direct determination of $\bar{v}_i - \bar{v}_j$ is impossible: the detector finds only a combined peak for two or more components, and its shape is indistinguishable from that of the individual components. Special relationships, allowing indirect measurement of $\bar{v}_i$ and $\bar{v}_j$, must then be used.

By applying the general theory of elution chromatography [78] to the separation of substances with closely similar properties, Glueckauf obtained [79] the following relationship between the separation of the components $i$ and $j$ and the elution volume $v$:

$$\ln Q_{ij} = \varepsilon_{ij} N \frac{\bar{v}_\Sigma - v}{\sqrt{\bar{v}_\Sigma - v}}, \qquad (28)$$

where $\bar{v}_\Sigma$ is the elution volume corresponding to maximum total concentration and $N$ is the number of theoretical plates in the column†. Glueckauf's expression can easily be converted into the form

$$\varepsilon_{ij} = -N \frac{d \ln Q_{ij}}{d \ln v}. \qquad (29)$$

The precision with which $\epsilon$ can be measured depends on the precision of the estimate of $N$ as well as on the precision of the measurement of separation as a function of volume. When the shape of the elution waves corresponds accurately to the normal Gaussian distribution the value of $N$ can be calculated [77] by the expression

$$N = 8\left(\frac{\bar{v}_\Sigma}{B}\right)^2, \qquad (28a)$$

where $B$ is the width of the peak at a concentration a factor of $e$ below the maximum. If the peak is distorted, on the other hand, it is better to use Keuleman's expression

$$N = 16\left(\frac{\bar{v}_\Sigma}{W}\right)^2, \qquad (28b)$$

where $W$ is the base of the triangle obtained by drawing two tangents through the points of inflection of the elution peak.

Two unsatisfactory aspects of Eqns. (28) and (29) must be pointed out. Firstly, the calculation of $\epsilon$ requires a knowledge of the differential of the degree of separation with respect to volume, involving at least ten measurements of $Q_{ij}$ for different fractions of the total peak. Secondly, these equations assume relatively large column lengths, in which the total capacity of the sorbent is large compared with the amount of material in the initial sample. Some expressions compatible with simpler experimental procedures are described below.

As before, we assume [82] that the individual peaks are in every way similar to the combined peak, i.e. we consider only very weak separations of the peaks. No assumption is made as to the shape of the peaks, and therefore no limitation is imposed on the size of sample in relation to the capacity of the column. According to this method, the concentration peak at the outlet of the column is divided into two parts containing approximately equal amounts of the mixture. These two parts are then analysed for the components. Consider the separation of a binary mixture. The general expression takes the form

$$\Delta x = x_t - x_h = \frac{(m_h + m_t) \cdot \varkappa_0 c_\Sigma \varepsilon (\bar{v}_\Sigma - v_0)}{\{m_t (1+\varkappa_0) + c_\Sigma \varepsilon [N - \varkappa_0 (1-N)] (\bar{v}_\Sigma - v_0)\}} \times \times \frac{1}{\{m_h(1+\varkappa_0) - c_\Sigma \varepsilon [N - \varkappa_0 (1-N)] (\bar{v}_\Sigma - v_0)\}}, \qquad (30)$$

where $x_t$ and $x_h$ are the mole fractions of the component in the tail and the head parts of the combined peak, $m_t$ and $m_g$ are the amounts of mixture in the same parts, $c_\Sigma$ is the total concentration at the point where the peak is cut, $\kappa_0 = x_0/(1 - x_0)$, $\bar{v}_\Sigma$ is the elution volume corresponding to the centre of gravity of the combined peak, $v_0$ is the free volume of the column, $N$ is the tail section of the base of the triangle $W$ (see above) defined by the tangents to the peak.

For $m_t \simeq m_h$ the expression simplifies to

$$\varepsilon = \frac{(1+\varkappa_0)^2 \cdot \Delta x (m_t + m_h)}{4 c_\Sigma \cdot \varkappa_0 \cdot (\bar{v}_\Sigma - v_0)}. \qquad (31)$$

Eqn. (30) can be generalised for the case of a multicomponent mixture, involving division of the peak into several parts [83].

## 2. Development and Frontal Chromatography Method

In the development chromatography method, the mixture to be separated moves along the column in the form of steady-state bands which retain their linear dimensions by virtue of a specially chosen set of conditions (initial form of the sorbent, presence of a desorbent). In a system of coordinates strictly related to the steady-state band, this method has the properties of a rectangular cascade operating in the total reflux regime [76,84]. Hence, all the expressions derived for the evaluation of $\alpha$ and $\epsilon$ in rectangular cascades are applicable in principle to the development chromatography method. The total reflux [84] and constant transfer [76] methods have been used in practice.

Separation by the frontal method is also described by rectangular cascade equations. The only difference from the development variant is that the band of varying concentrations (or band of concentration gradients) must now be treated as a rectangular cascade operating in the open mode [67,85].

# VIII. CRAIG'S METHOD (COUNTERCURRENT EXTRACTION)

The principle of the method is as follows [86]. We postulate a system containing a sufficiently large number of identical contact cells in series, which can be interconnected at will, and containing equal amounts of phase A. At time zero, we introduce into the first cell a volume of the second phase (B) containing two substances I and II, whose exchange with phase A involves linear distribution isotherms:

$$\frac{c_{IA}}{c_{IB}} = \lambda_1 \text{ and } \frac{c_{IIA}}{c_{IIB}} = \lambda_2.$$

After sufficient time, equilibrium distribution of the two substances between the phases will be established in the first contact cell. The mobile phase B is then completely transferred to cell 2, and the same volume of phase B

†An expression similar to Glueckauf's has been proposed independently [80]. However, the authors (who used the Mayer–Tompkins theory of chromatography [81]) treated elution as a stepwise process, and therefore their expression is inaccurate.

(without the substances to be separated) is introduced into cell 1. Equilibrium is again allowed to develop in both cells, and the equilibrium phase B is transferred from cell 1 to cell 2 and from cell 2 to cell 3, pure phase B being again added to cell 1. All these operations are then repeated the requisite number of times. The overall operation shows some close similarities to elution chromatography, from which it differs only in that the equilibration processes and the relative motion of the phases are separated in time, and the motion of the two phases is stepwise.

However, these differences are reflected only in the quantitative aspects of the problem. The distribution curves of the components after a sufficiently large number of steps look like elution chromatograms, and correspond to the normal Gaussian distribution. In common with elution chromatography, the method allows any number of components to be separated at the same time (Fig. 5). Furthermore, the Craig method is a more complex variant of the multistage condensation method, since the tail fractions of both phases are effectively subjected to multistage stripping, and their compositions must therefore obey the equations which describe this method.

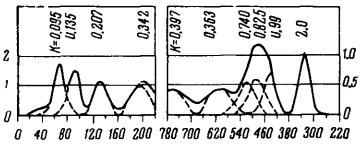



**Figure 5.** Distribution of aminoacids in a 220-cell Craig apparatus. From left to right, peaks correspond to tryptophan, phenylalanine, leucine, isoleucine, tyrosine, methionine, valine, α-aminobutyric acid, alanine, and glycine.

The theory of elution chromatography with stepwise motion of the mobile phase developed by Mayer and Tompkins [81] is fully applicable to the Craig process. This theory gives the relationship between the coefficients of the isotherms of the components, the ordinal number ($p$) of the volume of mobile phase, the ordinal number ($n$) of the contact cell, and the concentrations of the components in either phase.

Three methods of determining small separation coefficients in systems equipped with a sufficient number of contact cells can be distinguished.

1. By analogy with the elution chromatography method, we can use Eqn. (26), allowing however for the fact that $v_0 = 0$. According to Mayer and Tompkins [81], the maximum concentration of any component is achieved, for a given number $n$ of cells, after the passage of a volume $P_i = n\lambda$. The maximum values of $c_i$ and $c_j$ are related by

$$\varepsilon_{ij} = \frac{\overline{P}_i - \overline{P}_j}{\overline{P}_i}.$$

If $\epsilon_{ij}$ is large enough, $P_i$ and $P_j$ can be determined directly by any convenient analytical method, and a large number of contact cells is no longer required. But if $\epsilon_{ij} \ll 1$, it becomes possible to measure $\epsilon$ indirectly (as in Glueckauf's method). The concentrations of components $i$ and $j$ in the fractions of the mobile phase appearing at the outlet of the Craig system are related by the equation (in which $n$ = const)

$$\ln \frac{c_{ip}}{c_{jp}} = \ln \frac{\lambda_1}{\lambda_2}(p-1) + (p+n)\ln \frac{1+\lambda_2}{1+\lambda_1}. \quad (32)$$

After differentiation and some simplification we arrive at the expression

$$\ln \alpha = \frac{d \ln Q_{ij}\,(1+\lambda)}{dp}, \quad (33)$$

where $\lambda$ is the distribution coefficient for the combined substances $i$ and $j$.

2. If the Craig process is carried out with $p \leq n$ (i.e. no mobile phase is withdrawn at the outlet of the system), it is easy to show by means of the Mayer–Tompkins theory that the separation of the components in the two extreme cells (numbers 1 and $n$) are described by Eqn. (34). In this variant, the equality

$$p + n = p' + 1,$$

applies in any cell, where $p'$ is the total number of steps made in the system. Substituting this equality into Eqn. (32) we arrive at [76]

$$\ln Q_{ij} = (n-1)\ln \alpha; \quad \alpha = \frac{d \ln Q_{ij}}{dn}. \quad (34)$$

3. Lastly, as stated above, the end fractions of both phases undergo double multistage extraction in Craig's process, and therefore any of the expressions given above for the multistage condensation method can be used to calculate the separation of the components in the end fractions. In one sense, the Craig process is more economical (by a factor of two) than the normal double multistage condensation method. Half as many operations are needed to achieve a given separation, since one Craig operation results in the extraction of both end fractions.

The process has so far been applied only to the separation of substances by extraction, because the two phases can be separated rapidly and quantitatively with the apparatus developed by Craig and Past [87]. In principle, however, the method is applicable to any system including a mobile liquid phase, i.e. to the whole range of solution–sorbent systems. The main use of the method has been as a convenient laboratory means of separating substances and analysing mixtures.

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Mendeleev Moscow Chemical
Engineering Institute