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E. N. Lightfoot[a]; M. C. M. Cockrem[a]
[a] Department of Chemical Engineering, Madison, Wisconsin

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What Are Dilute Solutions?

E. N. LIGHTFOOT and M. C. M. COCKREM

DEPARTMENT OF CHEMICAL ENGINEERING
1415 JOHNSON DRIVE
MADISON, WISCONSIN 53706

ABSTRACT

An operational definition of recovery from dilute solutions is proposed, the major characteristic costs of such recovery processes are identified, and promising strategies for improving equipment and process performance are suggested.

INTRODUCTION

The purposes of this paper are to propose an operational definition of recovery from dilute solutions, to identify the characteristic major costs of such recovery processes and to suggest promising strategies for improving equipment and process design. Our primary concern is to provide guidance during the all important early stages of separations research, development and design when detailed cost estimates are not feasible.

Our underlying motivation is the need for more effective organization of separations as an engineering discipline, not only to facilitate the work of the designer but also to increase the effectiveness of research and long-range development in this important area.

More specifically we attempt here to define a compact family of processing problems closely enough related to justify grouping them together and important enough to make such a grouping useful. We then go on to ask the basic questions:

How do process economics scale with the concentration of the desired product in process feeds, and why?

How can one use the answers to this first question to improve equipment effectiveness and process economics?

Example:

As a particular example we consider the problem posed in Figure 1, where two processes for continuing removal of product from a fermentor are compared. The first is a direct contact between the fermentation broth and supercritical carbon dioxide, and the second is a modification in which a solid sorbent bed is placed between the fermentor and the supercritical extractor.

All experienced designers see advantages to the second of these possibilities, in part because a substantial volume reduction occurs before one uses the expensive high-pressure extraction. However, from a purely thermodynamic point of view the adsorbent bed appears to perform no useful function: it cannot increase the free energy of the desired product above that existing in the fermentor, and it is not likely that the free energies of the undesired species will be reduced significantly relative to that of the potential product.

This comparison then raises the two significant questions we shall examine in some detail below: how important is volume reduction, and should concentration and free energy be considered as independent parameters from an economic point of view?

CATAGORIES OF SEPARATION PROCESSES

Our first task is to narrow the scope of our analysis, and we must begin by recognizing that the cost of a separation process generally

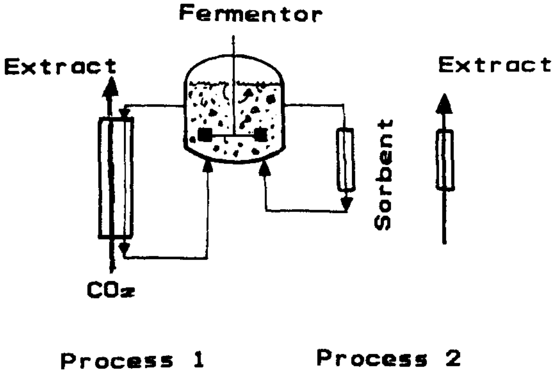


FIG 1. Comparison of two processes for the removal of product from a fermentor.

depends in a complex way upon the composition, temperature and pressure of each inlet and outlet stream.

However, there are a great many situations in which the values of feed and product streams depend primarily upon composition, and in which the number of such streams is small. We begin by restricting our attention to these and to considering three classes:

1) Concentration: increasing the concentration of a single potentially valuable substance originally present at low concentration in a mixture of undesired species. This is the situation of primary interest here.

2) Fractionation: separating two or more closely related species of comparable value, all initially present in economically significant amounts.

3) Purification: removal of a single undesired impurity from a mixture in which it occurs at a low initial concentration.

We now wish to contrast these three common limiting situations from an economic standpoint, to show that they are distinct, and, most particularly, to see if we can characterize the first in a useful way.

We begin by looking at Figure 2, what is commonly called a Sherwood plot, taken in this case from (1). Shown here is selling price per unit mass of various chemicals as a function of the reciprocals of their concentrations in the raw material or ore from which they were produced. Despite the wide variety of materials shown we find a surprisingly good correlation, long used to suggest the importance of separations costs. Sugar, penicillin and vitamin B_{12} are outliers, and it is reasonable to exclude these for the moment since the raw materials used as a basis of calculations for these, e.g. fermentation broth, have already undergone considerable processing.

Omitting these outliers we find that the correlation takes a simple linear homogeneous form expressible as:

$$\underline{C} = K\,\underline{W}_F \qquad (1)$$

where $\underline{C}$ = cost per kilogram of desired material (\$/kg),

$\underline{W}_F$ = mass of inert material in the feed per kilogram of desired material kg/kg),

and K = a "universal" constant, here about \$0.01 per kilogram of inerts (in 1984 prices).

This simple correlation has two important characteristics:

1)It suggests that processing cost is independent of the amount of the desired species present.

2)The correlation does not contain product composition.

The first of these characteristics is examined in detail below and is in fact the basis for much of our subsequent discussion. For the

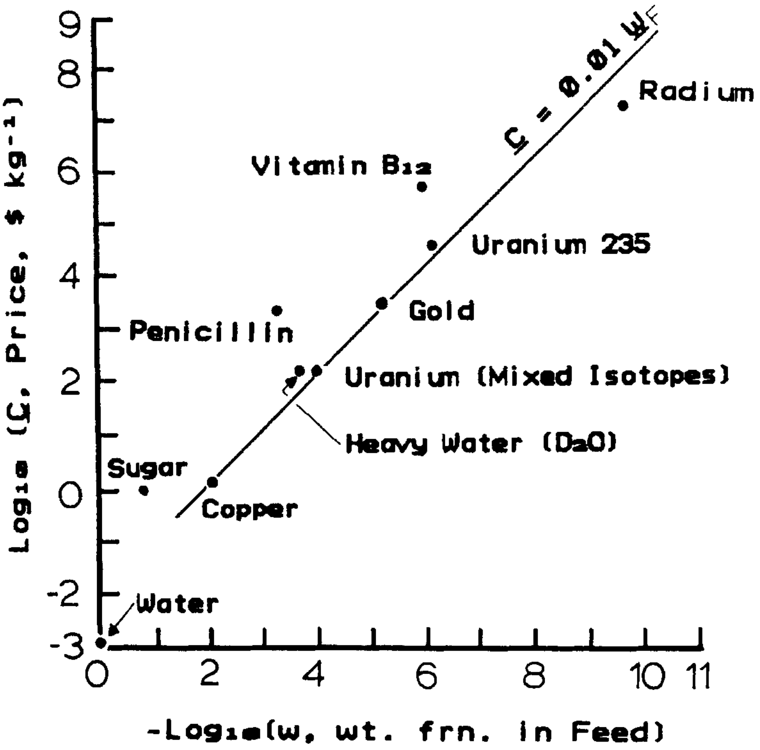


FIG 2. Costs of materials handling: Selling price as a function of weight fraction of desired material in the feed stream. Adapted from (1), originally found in (2), prices updated to 1984.

moment, however, we concentrate on the second and on comparisons between the economic characteristics of concentration, fractionation and purification.

We begin with purification, where costs commonly correlate according to the relation

$$\underline{C} = K' \ln [\underline{W}_F/\underline{W}_P] \qquad (2)$$

Here the subscripts $_F$ and $_p$ refer to feed and product conditions, respectively. This logarithmic relationship differs significantly from that of Eq. 1, and it also explains why product quality does not appear in this earlier equation: since the logarithmic dependence on concentration is much weaker than linear, purification costs tend to be small unless $\underline{W}_P$ becomes very small. This is indicated in Figure 3 where these two kinds of behavior are contrasted for a hypothetical

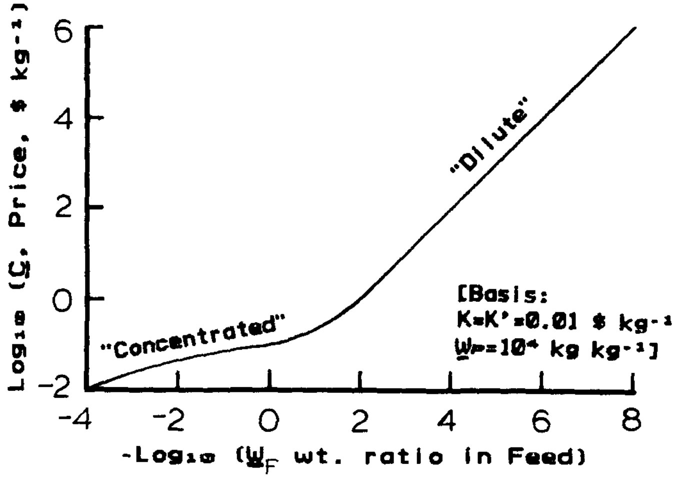


FIG 3. Recovery costs for dilute and concentrated solutions compared for a hypothetical situation.

situation: $K = K' = 0.01$, and $\underline{W}_P$ of 10^{-4}, corresponding to 99.99% product purity. We would thus expect "concentration" costs to dominate unless very high purity is needed.

Fractionation costs appear much more difficult to generalize, and we will not attempt to do so here. We shall only note that they tend to scale very differently with feed concentration than do concentration costs, and that they are dependent upon feed as well as all output compositions. Perhaps the best understood example is isotope fractionation where the Dirac concept of separative work (see for example (3)) appears to give an excellent correlation with separation cost. The scaling of uranium fractionation costs with "feed" composition is shown on Fig. 4 for the conditions and data of (3), which is a good source of information for isotope fractionation. Here a comparison with the data of Fig. 1 shows the marked difference in behavior between these two situations.

We find then that concentration, fractionation and purification do have distinct economic characteristics, and we are led to a definition of the first:

> We use the term concentration or recovery from dilute solution for those processes in which processing costs depend only upon the composition of the feed solution and are independent of the amount of the potentially desirable species present.

These processes are in a generalized sense transport limited in that processing costs are dominated by the processing of valueless constituents.

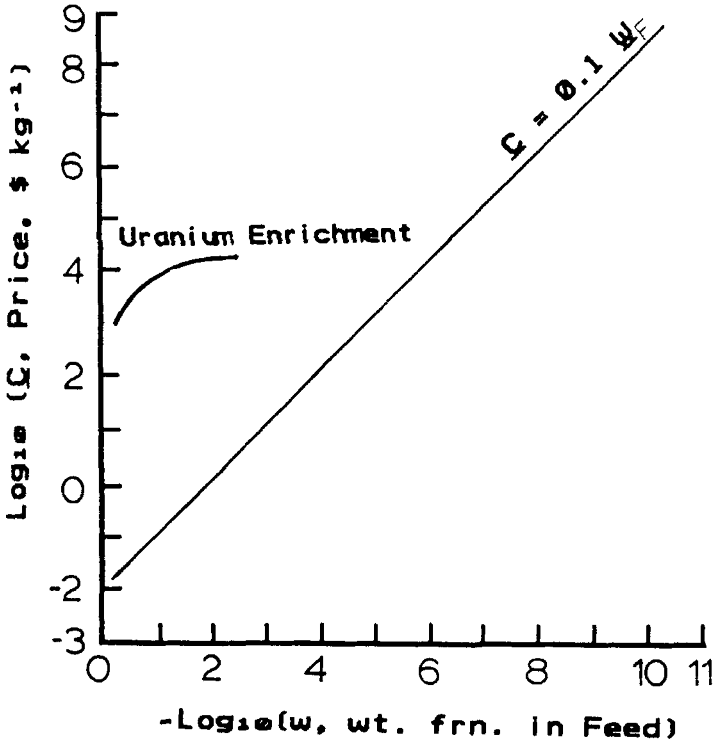


FIG 4. Fractionation (represented by Uranium enrichment, data from (3)) versus concentration (represented by trend line from Fig 2)

We now go on to investigate the utility of this definition and bases for its validity.

THE BASES OF DILUTE SOLUTION ECONOMICS

Here we begin by examining the cost-concentration relationships of chemicals not covered in previously available Sherwood plots and then go on to discuss their significance in terms of the physicochemical characteristics of the recovery processes used commercially.

Economic correlations: empirical evidence.

We begin by examining the "outliers" of Fig. 2, penicillin and vitamin B_{12}, along with a variety of other fermentation products in Fig. 5, a Sherwood plot prepared by Cockrem (4). In spite of considerable scatter the proposed trend line, Eq. 1 with

$$K = 0.1\ \$/\text{kg} \qquad (3a)$$

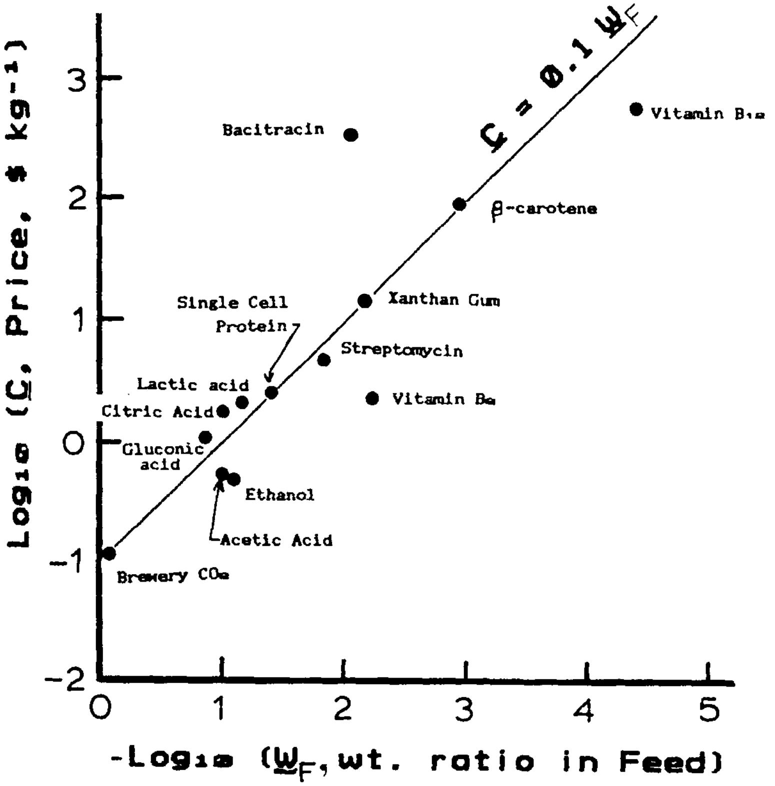


FIG 5. Costs for some currently economic or near economic fermentation products (Oct. 1984)

gives a good correlation. The higher value of K probably reflects the costs of fermentation as opposed to direct use of ores and commodity chemicals, predominating in Fig. 2.

Similar behavior was recently obtained for a wide variety of biologicals by Nystrom, as reported by Dwyer (5). These results, shown as Fig. 6, may be regarded as an independent verification of the proposed linear relationship, as neither author appears to have been aware of the Sherwood correlation. A linear correlation, corresponding to Eq. 1, but with a slope of -1 to conform to the interchange of coordinate axes, is seen to give a quite satisfactory fit up to a feed concentration of between 10 and 100 grams/liter. It gives a value of

$$K = \$0.3/\text{kg} \qquad (3b)$$

which is a bit higher than for the substances examined by Cockrem (4).

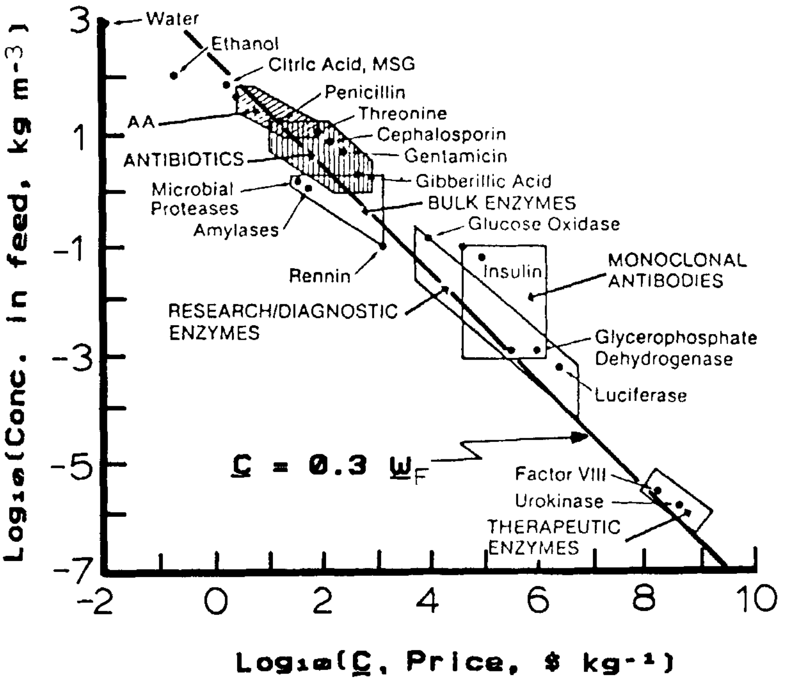


FIG 6. Selling price versus concentration in the starting material, from (5). Note that for dilute streams, log(conc. in feed, kg m^{-3} = 3 - log($\underline{W}_F$).

This apparently large difference is not really significant at the level of our analysis, which is really at the order-of-magnitude level. We find then that modifications of Eq. 1 fit these two sets of data and that both our observations and those of Nystrom (5) are compatible with our above definition of recovery from dilute solutions. However, it remains to consider the significance of these essentially empirical correlations, to see if other factors could be confounding our analysis. Among the possibilities are the costs of fermentation, incurred for most species shown in both figures, and the economies of scale.

The costs of fermentation and recovery are comparable for many of the commodity fermentations shown in Fig. 5, and the ratio of fermentation to recovery costs is estimated to be about 3:2 for the older antibiotics by Dwyer (5). Fermentation costs in turn can be quite different for different classes of products, but factors of two are only minor perturbations on the scales of our various Sherwood plots and would thus not be obvious on them. Moreover, the costs of fermentation for species resulting from secondary metabolism are not very sensitive to the amount of product actually produced, and we note, anticipating the arguments of the next section, that a fermentation dominated cost picture might scale according to Eq. 1 just as well as a recovery dominated one.

Such an ambiguity would not, however, occur for the much more dilute feeds toward the bottom right of Fig. 6, where Dwyer (5) estimates that recovery represents 80 to 90% of process costs. Here our original interpretation of Eq. 1 seems secure.

One must, however, also consider the economies of scale and the fact that more expensive materials tend to be manufactured in smaller amounts, hence less economically. It is not possible to evaluate this factor quantitatively, but such a possibility should once again suggest caution in interpretation of empirical correlations.

On the positive side it is the common experience of designers, based on detailed cost analyses, that initial volume reduction is highly desirable and that costs of separation steps decrease rapidly with the volume of fluid being processed.

We believe therefore that the above empirical correlations, and our accumulated experience, are sufficient to establish materials handling of unwanted constituents as major costs in recovery from dilute solution, and that they suffice to distinguish such processes from fractionation and purification. At the same time it is desirable to test this conclusion against physicochemical analysis and detailed cost estimates. We begin this process in the next section.

Physiochemical basis

Here we begin testing the above conclusions by examining some typical processes found in the early, presumably most expensive, stages of product recovery from dilute solutions. This must be considered as only a bare beginning to what should be a much more extensive analysis, but, as we shall see below, even such a preliminary analysis leads to potentially useful conclusions. We first consider filtration and allied processes, very often the first stage in a separation process, especially for biologicals, and then go on to liquid extraction and distillation, both very widely used, and, finally, to fixed-bed sorption and precipitation.

Filtration and Centrifugation. Especially for biologicals filtration and centrifugation are common early steps in the processing of dilute solutions. Typical applications include the removal of unwanted particulates, the recovery of desirable particulates and the removal of water and other solvents. Precoat filtration of mycelia from antibiotic broths is a particularly impressive historical example. Centrifugal separators are very widely used, and membranes for micro-filtration, ultra-filtration and reverse osmosis are currently getting a great deal of attention.

For all of these processes, cost is related only to the volume of broth or other suspending liquid and to the concentration and mechanical characteristics of mycelium or other solids present. It is not appreciably affected by the amount of potential product present, whether in the solution or suspended solids, if these are a minor constituent. Moreover, for individual classes of products at least, for example those produced from genetically altered E. coli, filtration characteristics are insensitive to the specific fermentation - at least to the degree of correlation shown in the above diagrams.

Filtration and centrifugation costs should then be proportional to the ratio of inerts to potential product, AND independent of the degree of purification later desired. Filtration costs do then behave consistently with the Sherwood plot and the explanation given for its cost/concentration relation given above. It may also be noted that these processes are transport limited in the full sense of this term.

However, the restriction to low concentration of valuable material in all streams must be noted; see discussion of sorption and precipitation below.

Liquid Extraction. Liquid extraction is another favorite early processing step, and, at first sight, it seems much more responsive to the amount of valuable material present: it is in principle possible to use highly selective solvents and thus to obtain rapid volume reduction proportionate to concentration of desired solutes. In practice, however, this is not normally true.

Available liquid extractors perform well only if the ratio of extract and raffinate streams is kept within relatively narrow limits. As a result examination of process data shows that volume reductions on extraction from dilute solution are typically five to ten fold, and that they very rarely exceed this latter limit, irrespective of the solute concentration of the feed. Processing costs, including solvent losses, are then again dependent only upon the amount of inert material present, for example water, and the process is again transport limited.

If solute activity coefficients are increased, as by addition of sodium or ammonium sulfate, this cost - including that of waste disposal - is again related to the mass of inerts rather than of desired solutes. Once again we find the Sherwood-plot economics justified.

Evaporation and Distillation. Evaporation is clearly the thermal analog of filtration, with the liquid-vapor interface taking the place of the filter septum and heat replacing mechanical energy. Hence similar comments apply, irrespective of refinements such as vapor recompression or multiple-effect operation.

The picture for fractional distillation is a bit more complex, but once again we find that, for sufficiently low feed concentration, costs should scale with mass of inerts rather than that of desired solutes. To demonstrate this we refer to Fig. 7, which is a McCabe-Thiele diagram for rectification of a binary mixture in which the desired constituent is the lower boiling but present in very low concentration.

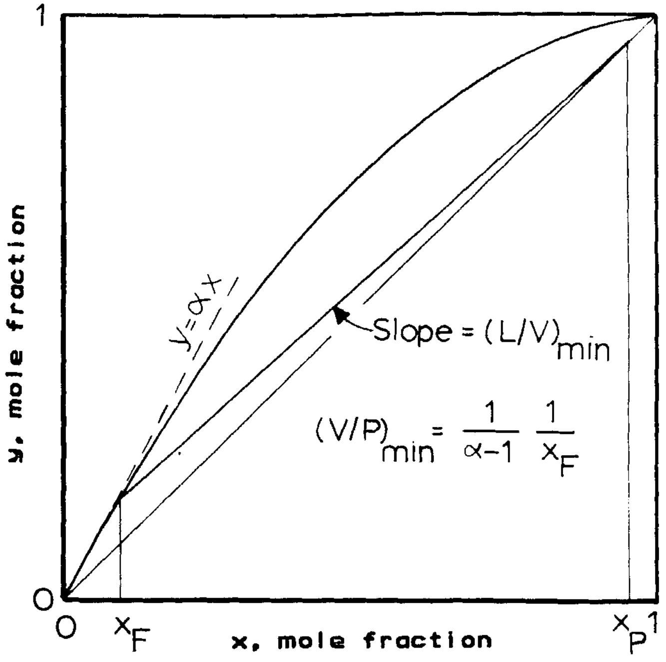


FIG 7. Distillation: Limiting reflux for dilute feeds.

More particularly it is assumed here that at the intersection of the "q-line" and the equilibrium line Henry's law applies in the form

$$y = a\,x \qquad (4)$$

where y and x are vapor and liquid-phase mole fractions, and a is the relative volatility at infinite dilution.

For simplicity we make the reasonable assumption that column operation is effectively determined by the minimum reflux ratio, noting that it is common to operate at 1.05 to 1.1 times minimum reflux. Now it is easily shown, by the usual material balance relationships, that, if the overhead is largely the desired solute

$$(V/P)_{min} = [1/(a-1)](1/x_F) \qquad (5)$$

where V and P are respectively the upflow vapor and product removal rates, and x_F is the feed mole fraction of the desired solute. It can, moreover, be shown that this conclusion is independent of the feed condition, i.e. the slope of the "q-line".

Moreover, since $(1/x_P)$ is very nearly the ratio of unwanted solvent to desired solute, and since P is about eqeual to the amount of desired solute in the feed to the column, we find

$$V \sim S \qquad (6)$$

where S is the mass flow rate of unwanted solvent in the feed.

We find then that vapor upflow rate, hence both capital and operating costs of the distillation, depend primarily upon the relative volatility and mass flow of solvent and, to the order of our approximations, are independent of the mass of solute. This is the situation required for our definition of recovery from dilute solution to be valid. Moreover, if the one disposable parameter, a, is changed, as by addition of salt to increase it, this cost as well will relate primarily to the amount of solvent present.

It is perhaps now time to put our basic idea to a more stringent test, and to do this we present actual cost data of Busche (6), FIG 8, for recovery of acetic acid from water by distillation on a Sherwood plot, along with a line of unit slope for reference. It may be seen that the predicted behavior is being approached for very dilute solutions, but that these are below the present economic recovery range of about 5 to 10%. Dilute by our standards in this system means below about 1%, and this is too low for economic recovery by any known means. It would be interesting to examine the Busche calculations to obtain insight into the nature of the cost-concentration relation shown here, but this is outside the scope of our present discussion.

Precipitation. We now consider direct precipitation of the desired material from solution, a technique which includes both the sulfate precipitation favored by biochemists and crystallization.

We see immediately that sulfate precipitation and any crystallization technique requiring a change in bulk solution thermodynamics give a cost picture which tends to be dominated by the amount of inerts present. However, filtration cost is related to the amount of product obtained, and our cost/concentration relations begin to become more favorable.

Moreover, if we can precipitate the desired solute by reversible reaction of a stoichiometric type, the cost picture becomes much more favorable. Examples include recovery of streptomycin (7,8) and riboflavin (9). In fact, as has long been known, this type of precipitation is the favorite among experienced process designers for recovery from dilute solution. We thus find here our first exception to Sherwood-plot economics.

Sorption Processes. Another favorite of designers working with dilute solutions is sorption of solute in fixed beds. Here the restriction on stream-rate ratios does not exist, and it is possible to find highly selective sorbents. One can often produce processes with solute-dependent costs.

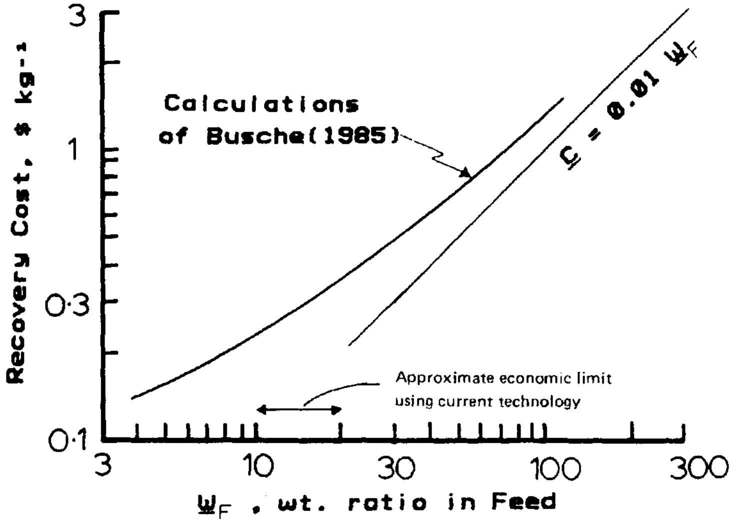


FIG 8. Costs for acetic acid recovery by distillation, from (6).

However, there are productivity limiting factors here as well which tend to related to mass of inerts: hydrodynamic resistance and bed saturation. In preparative HPLC for example, column productivity is often limited by high pressure drops and crushing strength of the packing. Moreover, bed capacity may be determined by sorption of inert materials which must be removed later. Both of these situations tend again to produce Sherwood-plot economics. It is not yet clear how such limitations affect the costs listed by Nystrom (5).

Summary. We find that the characteristics of most available solute concentration processes are consistent with the linear relation between process cost and mass of unwanted material found empirically, although the reasons for this common behavior differ significantly. These preliminary analyses thus confirm the dominance of materials handling costs in the recovery of potentially valuable materials from dilute solution. At the same time we find some possibilities for improving the cost/concentration relation using direct precipitation and fluid-solid sorption.

It remains to seek effective design strategies in the light of these conclusions and also improvements in equipment configuration. It is important to note that we have found serious drawbacks to both salting out, a favorite of chemists, and with distillation and liquid extraction, favorites of engineers. We now attempt to find promising alternatives and effective design strategies, in our concluding section.

STRATEGY AND REDUCTION OF RECOVERY COSTS

General Strategy.

The above discussion makes it clear that the sheer volume, or mass, of a dilute solution is a key characteristic, and that rapid volume reduction is important to economic design. It may also be seen that solute concentration and activity become independent parameters from an economic point of view and that the necessity of efficiently processing the entire feed stream is the most important single problem facing the designer.

We start by noting that both solute activity and concentration are important, and along with yield are the primary design parameters. It is clear for example that a saturated solution of gasoline in water has little economic value even though the partial molal free energies of the hydrocarbons are hardly distinguishable from those in pure gasoline. Similarly any solute tightly bound to an adsorbent is useless, however high its molar concentration.

It is therefore useful to plot the course of solute recovery on an activity/concentration diagram such as that shown in Fig. 9. Here a feed of low activity and concentration is to be converted to a nearly pure product approaching an activity of unity. One may take any of a large number of paths across this diagram, but the two shown are of particular interest:

1)The classic approach, especially favored by chemists, is to first increase the activity, to position I on the figure, and then to increase the concentration.

A familiar example is addition to the feed of Na_2SO_4 or $(NH_4)_2SO_4$, to bring solute activity up to - or even above - unity. The concentration can then be completed in any of several ways:
- i) Extract with even a poor solvent and back to water.
- ii) Precipitate, as by cooling or just allowing the solution to stand.

Such a procedure offers the advantages of simplicity: one need not find a highly selective solvent or precipitant. However, one must process large volumes to the end of the process, and use large quantities of salt. This salt in turn must either be recovered or disposed of in some acceptable, usually expensive, way.

2) A more economic approach is first to concentrate the solute from the feed, to intermediate E in the figure, and then to increase its partial molal free energy.

A simple example is the adsorption of an organic base, such as streptomycin, on an anion exchanging resin, and then eluting it with another anion or a stronger base.

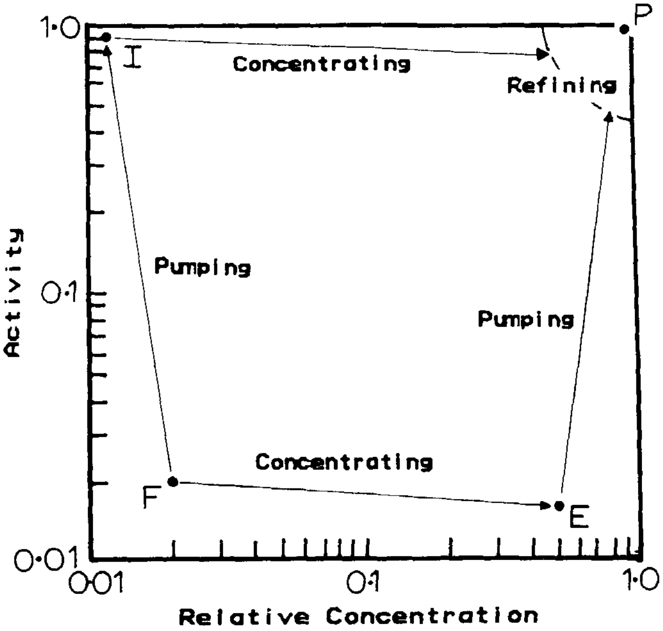


FIG 9. Solute recovery from dilute solution considered on an activity-concentration diagram.

Such a process offers the advantage of rapid volume reduction and is thus inherently superior to the first approach. However, it requires finding a selective extracting agent of high volumetric capacity whose affinity for the solute in question can be economically reversed. It thus requires a greater knowledge of system chemistry and more ingenuity.

The need to reverse selectivity presents particular difficulties, and there are basically only a few possible approaches:

Pressure "swings,
Temperature "swings",
Composition "swings" and
Electromagnetic "swings".

Each has its disadvantages. Pressure swings are limited to gases, and perhaps to protein molecules, which have anomalously large Poynting corrections. Temperature swings tend to produce relatively small changes in affinity, although they have been used to advantage in the recovery of citric acid (10). Chemical swings tend to consume large quantities of reagents, but they have yet to be thoroughly investigated. Electromagnetic effects have hardly been investigated at all, even though many processes such as electrodialysis have been proven feasible.

In the general case where there are large numbers of impurities present one should concentrate upon removing first those in largest amount and avoid burdening the concentration process with purification problems, unless such a combination can be obtained at low cost.

Whatever trajectory is taken in the a/c plane one must process the entire volume of the feed solution, and the restraints on this phase of the concentration process may be decisive. We now concentrate on this problem.

Improving Equipment Performance.

Processing of dilute solutions tends to be dominated by fluid mechanics problems: obtaining high volumetric throughputs and uniform flow distribution at acceptable pressure drops. However, in most instances one must also obtain high volumetric mass transfer rates and minimize dispersion, and it is therefore critically important to understand the different effects of geometry and flow regimes on momentum and mass transfer.

Flow dominated systems: removal and/or concentration of particulates.

Very often the first step in a recovery process is the removal of particulates, either an unwanted material such as a mycelial suspension or a desired concentrate such as a cell mass containing protein inclusion bodies.

If removal is by filtration the primary problem is the slowness of percolation through a particulate bed, described by the Blake-Kozeny equation

$$v_o = [(P_0-P_L)/L][D_p^2/150\,\mu][e^3/(1-e)^2] \quad (7)$$

where v_o = the superficial percolation velocity,

P_0 and P_L = the upstream and downstream motive pressures respectively,

L = bed thickness,

$D_p = 6/A_v$ = mean particle diameter,

A_v = total specific surface of particles in bed,

μ = fluid viscosity and

e = fractional void space of bed.

The great sensitivity of percolation velocity to particle diameter is of primary importance, but the effect of void fraction is also large, especially for the common case of deformable particles.

If removal is by centrifugation the problem is the low terminal velocity of small particles,

$$v_t = (1/18)\,D^2\,(\rho_s - \rho_f)\,g_{eff}\,/\,\mu \quad (8)$$

where D = equivalent spherical diameter,
ρ_s and ρ_f = solid and fluid densities, respectively,
g_{eff} = total body force per unit mass acting on the particle.
Again particle diameter appears to the second power.

Both precoat filters, to decrease effective bed thickness and increase effective diameter and void fraction, and centrifuges have been widely used, particularly in the fermentation industry. They have proven to be very expensive, and there has been much interest in membrane microfilters designed to keep bed depths small via vigorous cross flow at the menmbrane surface. Filter and centrifuge design appears to be mature, but membrane devices are less well investigated and probably offer better prospects for improvement, especially if more advantage is taken of available fluid mechanic theory.

There are, however, other possibilities which should be considered seriously.

Magnetophoresis in a high-field/high-gradient magnetic filter of the type sketched in Fig. 10 offers the possibility of high throughput with easy washing and unloading, and such devices have been used successfully with a wide variety of suspensions. For example the adsorption of small amounts of magnetic iron oxide on biological particulates has been successful in clarifying lake water. Concentration of immobilized particles in bed interstices minimizes their effect on pressure drop, and use of magnetic forces increases removal efficiency.

There is also the possibility of avoiding particle removal where the valuable constituent is in the suspending fluid. The use of magnetic bed stabilization (11) permits expansion of a granular sorbent bed sufficiently to permit passage of small particulates without seriously compromising mass transfer. One may also use sorbents with minimal form drag, as discussed further below for the same purpose. Neither of these possibilities appears to have received the attention it deserves, although magnetically stabilized beds are beginning to be used for other purposes (12,13)

Combined flow and mass transfer: transport capacity. Almost all recovery processes require effective mass transfer between two partially miscible phases, and normally the degree of segregation is insufficient to permit batch contacting. One must then normally use a close approach to counterflow, and this requires high volumetric mass transfer coefficients, low dispersion in the flow direction and good uniform lateral distribution. These conditions usually demand long narrow columns of small packing or sorbent particles, and these typically have limited flow capacity.

The problem of lateral distribution is difficult to treat systematically at present, but the balance between mass transfer effectiveness and throughput can be improved by utilizing the much greater sensitivity of momentum than mass transfer to system geometry. More specifically one wishes to maximize mass transfer while minimizing momentum transfer, i.e. to maximize the Chilton-Colburn "j-factor" for

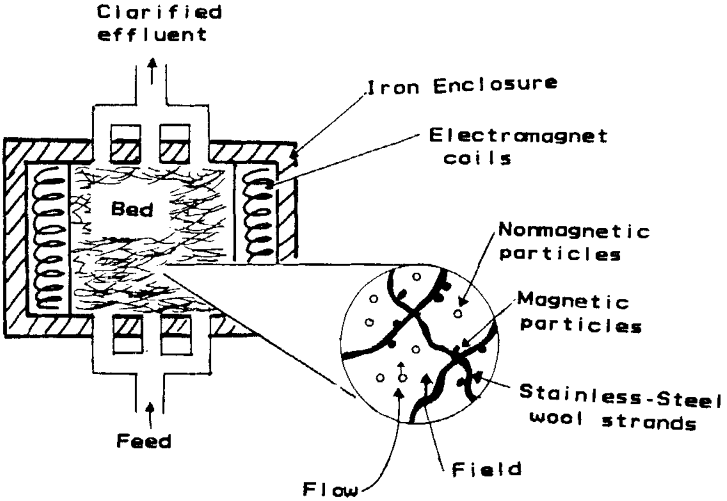


FIG 10. Magnetic filtration using a cyclic high-gradient magnetic separator.

mass transfer relative to its momentum transfer analog, one-half times the friction factor (14). The most effective way to obtain a low ratio of f/2 to j_D in turn is to avoid form drag to the degree possible. We illustrate this by considering two specific cases.

a. Systems at high Reynolds numbers.

We begin here by looking at the simplest case of solid-fluid mass transfer.

Most large-scale mass transfer processes of this type operate at the high Reynolds numbers where laminar boundary-layer theory is valid, and here we find a remarkable insensitivity of mass transfer effectiveness to geometry whereas the sensitivity of momentum transfer is large. This is shown in Fig. 11 where friction factors and j-factors are shown for a variety of objects as a function of Reynolds number, using the length of the object in the flow direction as reference length.

It may be seen that all of the mass-transfer data fall in a narrow band which can be approximated as

$$j_D = (2/3)\ Re^{-1/2} \qquad (9)$$

The same is true for f/2 in the absence of form drag, to the accuracy of Eq. 8. We find then that the lowest attainable ratio

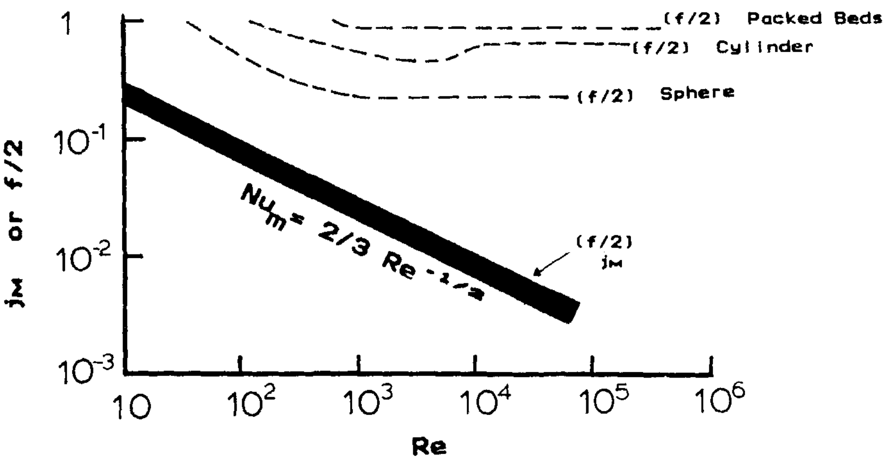


FIG 11. Area-mean Chilton-Colburn j-factors and Fanning friction factors for forced convection past submerged objects. The band of j_M and f/2, approximated by $Nu_M = 0.66\ Re^{-0.5}$, includes j_M and f/2 for flat plates and spinning disks, but only includes j_M for spheres, cylinders and packed beds. Adapted from (15).

$$(f/2j_D)_{min} = 1 \qquad (10)$$

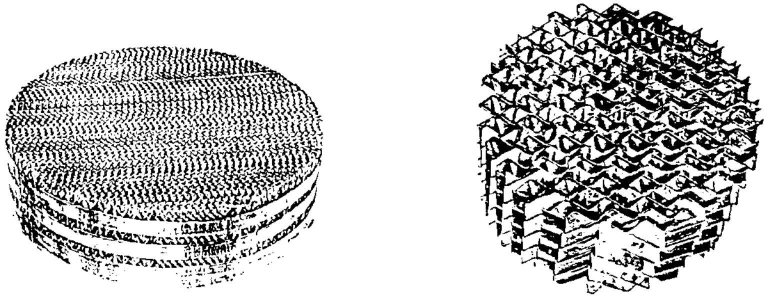
and this is just what we would expect from available asymptotic analyses. However, in the presence of form drag this ratio is seen to be much higher, often by two orders of magnitude, and this increased form drag produces no appreciable increase in mass-transfer effectiveness.

The lesson is clear: form drag should be avoided to the extent physically possible, unless it produces other major advantages, for example improved flow distribution.

The situation for fluid-fluid mass transfer in packed columns is much more complex, and there is too wide a variety of situations to be considered here. The basic message is, however, much the same, and it is borne out in practice by the success of a variety of high-performance packings. The Sulzer Flexipac shown in Fig. 12 is a good example. Here the primary packing elements are all cylindrical surfaces showing minimal form drag once the fluids have entered the packing channels.

b. Systems at low Reynolds numbers.

Fixed-bed sorbers almost always operate at very low Reynolds numbers, where one may assume creeping flow, and the same will probably



A. Koch-Sulzer Packing: Woven gauze

B. Koch Flexipac™ Packing: Corrugated Sheets

FIG 12. High-efficiency high-capacity packings for mass and heat transfer. The Koch-Sulzer packing is for low liquid flowrates and the Koch Flexipac packing is for high liquid flowrates (16).

be true of many related operations, such as use of magnetically stabilized moving beds, which have yet to be fully developed. In many cases, for example high performance liquid chromatography now being considered for large-scale operation, pressure drops are so high as to approach the deformation and even crushing limits of the packing, and performance is truly flow limited.

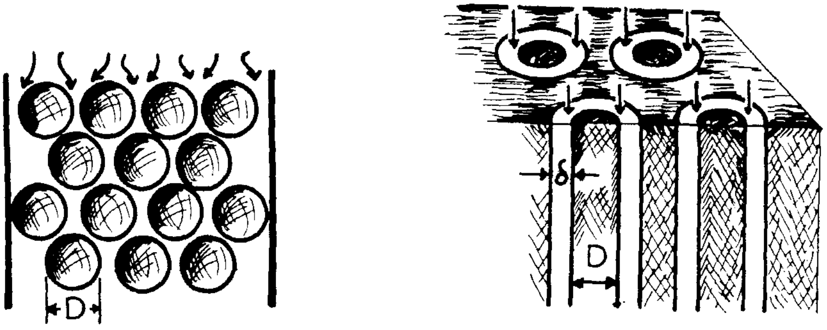
It is therefore again important to minimize momentum transfer relative to mass transfer, but it is now convenient to define the ratio of these quantities in terms of Nusselt numbers for mass transfer and the momentum transfer analog Ref/2. There are again many possible situations, and we confine ourselves here to those, quite common in practice, where mass transfer resistance is predominantly in the solid phase.

We again find form drag to be avoided, and we illustrate this by comparing a spherical packing with one of the most easily realized form-drag free geometries, bundles of parallel cylinders. Such a system is sketched in Fig. 13, and for simplicity we assume the active portion of the cylindrical solid phase to be a thin shell within which curvature can be neglected. Friction factors for these two systems are readily available, and we calculate that for the spherical packing using a void fraction of 0.4. Then:

$$Ref/2 = 211 \quad \text{(sphere)} \qquad (11)$$

$$= 8 \quad \text{(cylinder)} \qquad (12)$$

Asymptotic mass transfer coefficients can be calculated using the zeroth approximation of Reis et al (17), and corresponding Nusselt numbers are obtained using the sphere and cylinder diameters as reference lengths.



Spherical Bead Packing **Annular Cylinder Packing**

Fig 13. Two geometries to be compared for resistance to fluid flow and to mass transfer: Spherical bead packing with beads of diamter D, and annular cylinder packing with a thin shell of thickness o and cylinder diameter D.

We thus obtain:

$$Nu_{asym} = 10 \quad \text{(sphere)} \tag{13}$$

$$= 3\, D_{cyl}/\delta \quad \text{(cylinder)} \tag{14}$$

It follows that

$$[Ref/2]/Nu_{asym} = 21 \quad \text{(sphere)} \tag{15}$$

$$= (8/3)(\delta/D) \quad \text{(cyl)} \tag{16}$$

Then the resistance ratio for spheres is about one to two orders of magnitude higher than that for cylinders, depending upon the thickness of the active layer δ in the latter.

When one recognizes that cylinders offer the additional possible advantage of mechanical support by an imbedding matrix one sees an enormous potential advantage for this latter geometry, almost certainly enough to justify the expense and uncertainty of a commercial development.

Improving Separation Chemistry.

The development of economic recovery processes depends heavily upon the identification and preparation of extractants which have high selectivity, capacity and reversibility. In any individual case this means that we need improved methods of predicting solubility under a wide variety of conditions. Even for chemically simple systems such as

BULK FLUIDS	SURFACES	HOLES
......EXAMPLES......		
partition	adsorption	zeolites microporous gels
......CAPACITY......		
High	Low	Moderate (to high ?)
......SELECTIVITY......		
Low	Higher	Highest (?)
......FORCES INVOLVED......		
intermolecular	intermolecular orientation	intermolecular orientation size shape

..SKETCH OF CONCENTRATION GRADIENTS
NEAR THE MASS TRANSFER INTERFACE...........

FIG 14. Rules of Thumb and thermodymanic polarization.

the low molecular weight oxychemicals this means replacing presently available group contribution methods, but the challenge is even greater for more complex substances such as proteins. Such thermodynamic research is beyond the scope of this analysis, but a modest general speculation may be in order. We therefore consider here the relative merits of true liquids, adsorbents and microporous gels as extractive agents, and we illustrate their salient characteristics in Fig. 14.

The first two classes are the most familiar to chemical engineers, and it is a widely used "rule of thumb" that liquids have the higher capacity and adsorbents the higher selectivity, so that neither has the desired combination of capacity and selectivity. There seems to be a good basis for this empiricism, inherent in the basic morphologies: the low capacities of adsorbents result from the need to have a macroscopic mechanical support for the active surfaces, which however only attract a sorbate layer of molecular dimensions. The lower selectivity of liquids results from the higher mobility of disssolved as opposed to adsorbed molecules so that orientation effects are much less important than for adsorbents: liquid selectivity depends primarily upon intermolecular forces.

Microporous gels on the other hand offer the possibility of high capacity and selectivity, and also interesting possibilities for reversibility. High capacity is possible because the pore "walls" are of molecular dimensions, and the enclosed space can be comparable to that occupied by the matrix. Selectivity now depends upon pore size and shape as well as orientation and intermolecular forces and should therefore be superior to either liquids or adsorbents. Reversibility can now be achieved by changing either pore dimensions, as by swelling, or interior chemistry, as by ion exchange. Affinity chromatography and its variants are examples of current interest which remain an art but should be put on a more systematic footing. These properties have been utilized, most recently for example in salt gradient elution, but many interesting possibilities remain unexplored.

Since solid sorbents also have many advantages from a fluid mechanical stanpoint they appear very promising and should be vigorously investigated.

It is also important to give serious consideration to chiral and other inclusion compounds, for example ionophores, which offer similar advantages and in addition the possibility of selective precipitation - the favorite primary recovery technique of all experienced designers.

SUMMARY

Examination of crude economic data suggests that recovery of potentially valuable solutes from dilute solution is dominated by the costs of processing large masses of unwanted material. This suggestion is confirmed by examination of the most widely used current processing techniques, and a general strategy is suggested for reducing recovery costs. Important to this strategy is rapid volume reduction, long recognized as important by experienced designers. Specific means are also suggested for reducing the costs of individual operations. Important among these are the reduction of flow resistance, increased use of solid sorbents and more dependence upon chemical selectivity.

NOMENCLATURE

Roman

A_v	total specific surface particles in bed ($m^2\ m^{-3}$)
$\underline{C}$	cost of desired material as a concentrated product (\$ kg^{-1})
D	equivalent spherical diameter (m)
D_{cyl}	diameter of cylinder (m)
D_p	mean particle diameter (metre) $D_p = 6 / A_v$
g_{eff}	total body force acting on particle per unit mass ($m\ s^{-2}$)
K'	universal constant, a measure of the costs associated with processing a type of raw material (\$ kg^{-1})
L	bed depth (metre)
P_o	upstream motive pressure (Pa)
P_L	downstream motive pressure (Pa)
P	molar rate of product removal (mol s^{-1})

S	mass flowrate of unwanted solvent (kg s^{-1})
v_t	terminal velocity of particle (m s^{-1})
v_o	superficial percolation velocity (m s^{-1})
V	molar rate of upflow (mol s^{-1})
w	weight fraction of desired material in the feed stream
$\underline{W}_F$	mass ratio of inerts to desired material in feed, = (1-w)/w
$\underline{W}_P$	mass ratio of inerts to desired material in the product stream
W_P	mass ratio of desired material to inerts in product stream, = $1/\underline{W}_P$
x,y	mole fraction of desired solute in liquid or vapor phase
x_F	mole fraction of the desired solute in the feed

Greek

a	relative volatility at infinite dilution (-)
δ	thickness of annular region around a cylinder (m)
e	fractional void space of the bed (-)
u	fluid viscosity (Pa s)
ρ_s	solid density (kg m^{-3})
ρ_f	fluid density (kg m^{-3})

Dimensionless groups

f	friction factor for fluid flow
j_D	Chilton-Colburn j factor for mass transfer
Nu_{asym}	asymptotic limit of the Nusselt number for mass transfer
Re	Reynolds Number

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