

How to Design Fractional Crystallization Processes

When a chemical engineer is asked to design a distillation process for separating a complex mixture of components, he goes about it systematically and confidently. He can recognize many different cases, or configurations of equilibrium lines, and knows how to deal with each. Considerable ingenuity may be required, but the engineer knows the "tricks of the trade" and how to attack the problem.

Faced with a mixture of components to separate by fractional crystallization, however, he usually has little to fall back on except intuition and inspiration. Fractional crystallization is not more complicated than distillation, but the engineer has not been taught any principles from which to recognize formal similarity in different examples. And he seldom has any stock of standard process solutions for given cases when he meets them. Design of even moderately complicated fractional crystallization processes is recognized as beyond the ordinary skill of a chemical engineer—"one versed in the art"—in that they can usually be patented.

But rational principles and a bag of tricks do exist for fractional crystallization. With these in mind a process designer knows in advance what to look for in a phase diagram, and what to do when he finds it. He can move ahead as deliberately as if he were treating a distillation problem rather than having to look for inspiration.

This paper focuses upon a set of systematized procedures by which ideal equilibrium processes can be generated from solubility data. There is not space in a

single article to treat also the manifold problems encountered in reducing an ideal process concept to a practical and economical flowsheet. But a process must be conceived in principle before it can be reduced to practice, and it is in the original conception of processes that most engineers have least background.

The paper is divided into three sections, corresponding to handling three, four, and n components, respectively. Since a three-component system is a special case of a four-component one, and both are special cases of n component systems, this necessitates passing from special to general cases, with repetition of basic ideas in progressively more generalized form. But with each increase in the number of components, the abstractness and difficulties of representation and treatment increase greatly. The paper is arranged this way primarily so that an engineer faced with a specific fractional crystallization problem need go into the subject only as deeply as necessary to solve his problem. He won't have to cross mountains to climb a foothill.

THREE-COMPONENT SYSTEMS

Fractional crystallization processes are worked out graphically in practice, since solubility data are highly empirical at this time. Graphical methods are used to represent the system, its equilibria, and the results of various process manipulations. We now start laying the foundation for graphical treatment in terms of the three-component systems being considered here.

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Composition plots. The composition of a three-component system has two degrees of freedom, and can be represented in a two-dimensional coordinate system or graph. If the components are designated respectively A , B , and S , $\%A$ can be plotted against $\%B$. The content of the third constituent, S , is always determined by the condition $A + B + S = 100\%$. Any weight units may be used. In this paper we use simple wt $\%$ extensively (weight of a given component per 100 weights in total system). Equivalent wt $\%$ is used occasionally (equivalent weights of a given component per 100 equivalent weights of all components in system).

Other composition ratios might be used, such as grams per 100 grams solvent, grams per 100 grams "free" solvent, or grams per gram of key component other than solvent. Such plottings are in some cases very convenient, but are not fundamentally different from percentage plots. Concentration plots (grams per liter) are not suitable because they do not permit use of constructions to be described below.

Composition coordinates may be either rectilinear or skewed. A percentage plot will be bounded by a right triangle in rectilinear coordinates (Figure 1). If the axes are 60° apart and the scale modules are equal, the familiar equilateral triangular plot appears (Figure 2). It has no functional advantages over one using rectilinear coordinates, being just a linear transformation from it. The two can be used interchangeably (9), and we will use them that way.

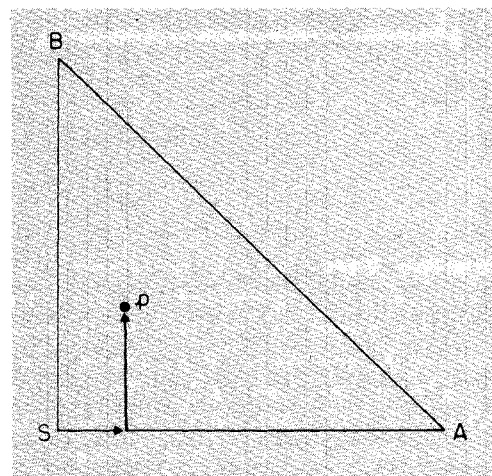


Figure 1. Plotting composition point in right angle coordinates

It will be convenient to think of compositions as being represented by vectors, and coordinate axes as bases for vector spaces. Thus point p (Figures 1 and 2) represents the sum of a constituent vector in the A direction representing the $\%$ of component A , and one in the B direction representing the $\%$ of B . In this view coordinate axes are simply guidelines showing the direction and scale modules of A and B vectors. Such a view is perhaps overelephant for simple systems, but it becomes useful in dealing with more complicated ones.

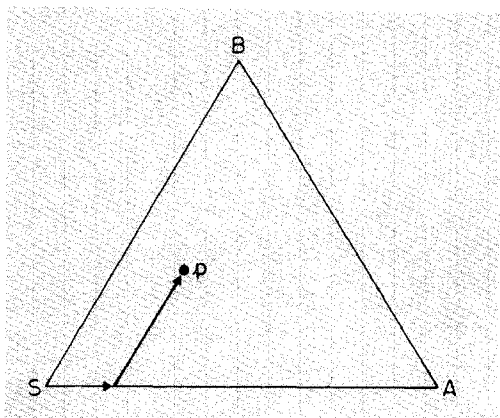


Figure 2. Plotting composition point in 60° or triangular coordinates

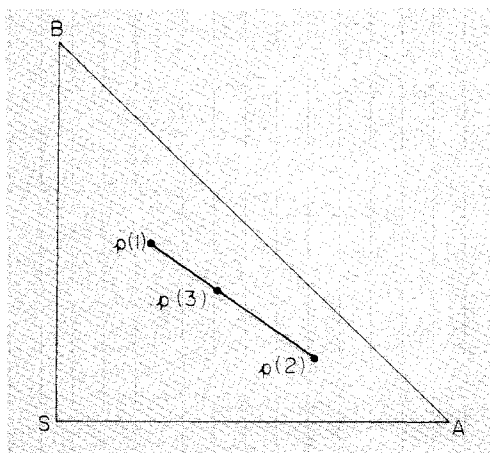


Figure 3. "Center of gravity" principle

Construction lines. If any two systems 1 and 2, having compositions represented by $p(1)$ and $p(2)$ (Figure 3), are mixed to form another system 3, the composition of the new system, $p(3)$, will be on a straight line joining points $p(1)$ and $p(2)$. This derives from material balance, and holds also for the case that system 3 is split into systems 1 and 2. Such straight lines form the bases for all process constructions on a composition diagram.

It follows from the above that if solvent is added or subtracted from any system, the residue must plot somewhere along a ray from the origin or solvent point. Such rays will be called "dilution rays." Likewise, adding or subtracting solids A or B will move the system composition point along rays through points A or B, respectively, and these will be called "A rays" or "B rays" or "solid rays" (Figure 4).

Material balances. Material balance calculations are made from process constructions by the method known as "center of gravity" (9), or "line segment ratio" (8), or "ratio scale moment" (5). For any case in which

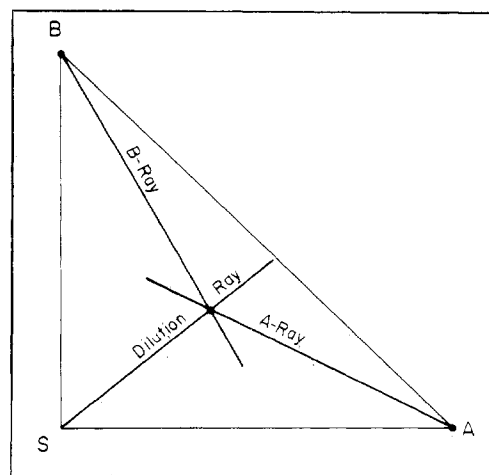


Figure 4. Construction "rays"

$$A(1) + A(2) = A(3) \quad (1)$$

$$C(1) + C(2) = C(3) \quad (2)$$

it follows algebraically that

$$\frac{C(2)}{C(1)} = \frac{\frac{A(3)}{C(3)} - \frac{A(1)}{C(1)}}{\frac{A(2)}{C(2)} - \frac{A(3)}{C(3)}} \quad (3)$$

Equations 1 and 2 may be interpreted as a material balance of two constituents or groups of constituents in systems 1 and 2, combining to form system 3. A 's may be interpreted as weights of component A; C 's may be interpreted as hundred weights of components A + B + S. Then Equation 3 interprets as

$$\frac{\text{total weight from system 2}}{\text{total weight from system 1}} = \frac{\%A \text{ in mixture 3} - \%A \text{ in system 1}}{\%A \text{ in system 2} - \%A \text{ in mixture 3}} \quad (4)$$

The mathematical relationships are analogous to those of levers or moments. Material balances may be figured as though the line joining systems 1 and 2 on the chart were a lever arm, with "basis" weights (weight of components comprised in the denominators of the composition ratios) contributed by the various systems applied at their system points. The mixture will lie at the "center of gravity" of the contributing systems. Alternatively, moments may be taken around any one of the three system points. The moments contributed by the other two must be equal.

Thus taking moments around point $p(1)$ (Figure 3)

$$(\text{total weight in system 3}) \times (\%A \text{ in system 3} - \%A \text{ in system 1}) = (\text{total weight from system 2}) \times (\%A \text{ in system 2} - \%A \text{ in system 1}) \quad (5)$$

If we wanted to calculate directly the distribution of component *B* between the three systems, its weight would be put into the denominator of a composition ratio.

Thus

$$\begin{aligned}
 &(\text{wt } B \text{ in system 3}) \times \\
 &\left(\frac{\%A}{\%B} \text{ in system 3} - \frac{\%A}{\%B} \text{ in system 1} \right) = \\
 &(\text{wt } B \text{ from system 2}) \times \left(\frac{\%A}{\%B} \text{ in system 2} - \right. \\
 &\quad \left. \frac{\%A}{\%B} \text{ in system 1} \right) \quad (6)
 \end{aligned}$$

Equilibrium lines—The phase diagram. At equilibrium, a system of any given composition will be made up of one or more phases. The phase diagram is a set of equilibrium curves on a composition plot showing what these phases are. In fractional crystallization, equilibration is conceived to take place only if a solution phase is present. Therefore, the phase diagram is concerned mostly with compositions of the liquid phase, and is often called a “solubility diagram.”

Various types of phase diagrams will be discussed in more detail in the sections that follow.

Classification of phase systems. Fractional crystallization systems comprise solutes that are to be separated, and a solvent from which they are selectively crystallized. For verbal convenience the former will sometimes be called “salts,” and the latter “water,” letting these specific materials stand for their respective classes. Three basic types of systems are recognized:

Type I: Solutes crystallize without forming either solid solutions or compounds among themselves (double salts). They may, however, form compounds with the solvent (hydrates)

Type II: Solutes crystallize as compounds (double salts)

Type III: Solutes crystallize in solid solutions

Space does not permit treatment of Type III systems in this paper. We note, however, that the separation methods used in such systems are analogous to those for liquid-solid extraction.

Type I Systems

The phase diagram for a Type I system at some temperature *T*(1) might appear as in Figure 5. Solutions plotting along curve *a*(1)–*b*(1) are saturated with respect to component *A*; those along *b*(1)–*c*(1) with component *B*. Systems plotting within the solution phase bounda-

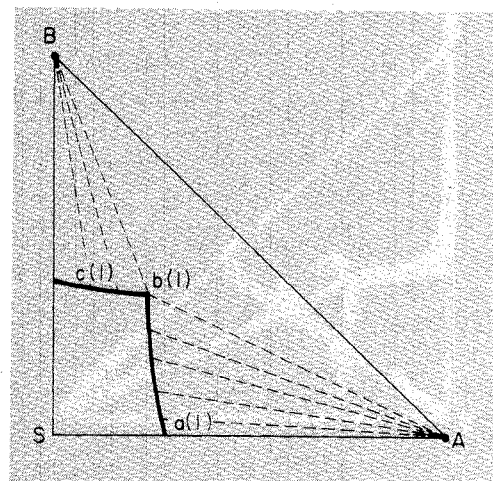


Figure 5. Typical solubility diagram—Type I

ries *S*–*a*(1)–*b*(1)–*c*(1) consist of unsaturated solution and no solid phase. Systems plotting outside the boundaries comprise saturated solution and whatever solid phases must be split out to yield saturated solution as the residue.

A-level separations. Any mixture of *A* and *B* having a ratio *A/B* different from that of point *b*(1) can be resolved at temperature *T*(1) into a mixture of solution and a crop of crystalline *A* or *B*, whichever is in excess, by adding or evaporating solvent. Thus in Figure 6, solvent may be added to a mixture of solids plotting at *F*, moving the system point along a dilution ray toward the origin or solvent point. With proper adjustment of solvent, the system can be brought to plot at point *a* on a tie line between the compositions of doubly saturated solution at *b*(1) and that of the crystalline species *A* containing component *A*. (If *A* crystallizes in pure form its solids point will be at 100% *A*. If it crystallizes as a hydrate, its solids point will be less than 100% *A*. If it is impure, it will plot off the *A* axis.) After equilibration the system will consist of a phase of *A* solids, and a solution of composition *b*(1). And while arranging to have the solution phase arrive at *b*(1) will give the greatest yield of crystalline *A*, dilution of the system to any point between *a* and *c* will result in a solution phase saturated with respect to *A*, and a solid phase of species *A*.

System *a* can be reached by leaching solids with the appropriate amount of solvent, thus dissolving all *B* and as much *A* as is needed to form solution *b*(1), leaving excess *A* undissolved. Alternatively, it can be reached by diluting to or beyond the point *c* to dissolve all solids, and then evaporating to system point, *a*, whereby excess *A* is recrystallized. Or, if the system initially contains excess solvent, it can be brought to point *a* by evaporation. Any route leaves a crop of solid phase *A* that can be physically separated, and a solution *b*(1) that must be fractionated.

Such separation of a crop of one constituent is basic to all fractional crystallization processes, and will be called an *A*-level separation.

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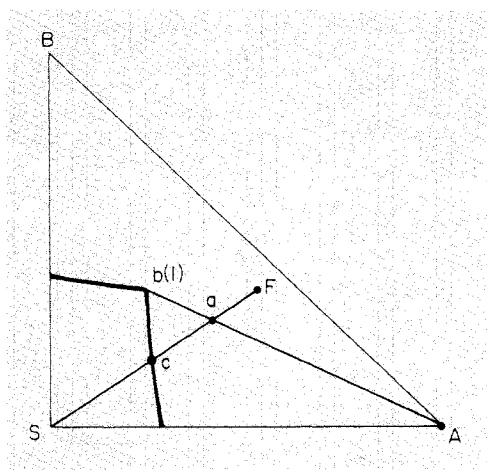


Figure 6. A-level separation

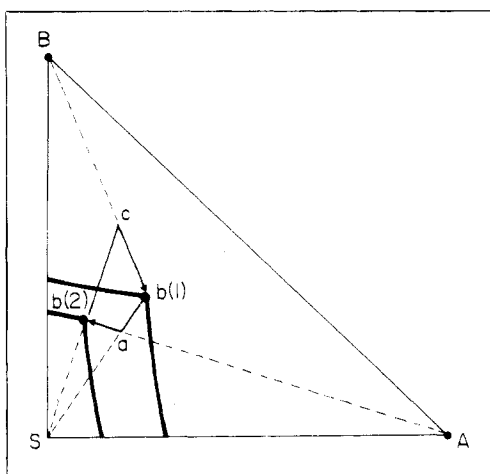


Figure 7. B-level cycle

Basic Type I fractionation cycle. The solubility isotherm for another temperature $T(2)$ has been added in Figure 7. The doubly saturated point, $b(2)$, has moved to a lower A/B ratio than it had at $T(1)$. Therefore the following generalized cycle is possible:

- (1) Starting with solution at $b(1)$, change the temperature to $T(2)$ and adjust the solvent concentration (in this example dilute) to reach system point a . This results in an A -level separation yielding $b(2)$ solution and a crop of crystal species **A**. Separate crop of **A**.
- (2) Change temperature of solution $b(2)$ to $T(1)$, adjust solvent concentration (in this example evaporate) to system point c . This makes an A -level separation yielding a crop of solid phase **B** and a solution phase of composition $b(1)$. Separate the crop of **B** and recycle the solution to step 1.

Existence of this cycle assures that we can fractionate any Type I, three-component system unless points $b(1)$ and $b(2)$ have the same A/B ratio. The chances

of finding a system in which all points along the polytherm have the same A/B ratio seem infinitesimal. Therefore, in principle, any Type I, three-component system can be separated by fractional crystallization. For future identification, we call this cycle a B -level separation.

To be economical, the basic cycle should have short dilution and evaporation vectors $b(1)-a$ and $b(2)-c$ so that there will be a small amount of solvent to add and evaporate. It should have long crystallization legs $a-b(2)$ and $c-b(1)$ to give a high yield per cycle.

Standard Type I process. The cycle just described depletes the system. Some A and B are removed each cycle, and none are added back. A continuous or steady-state process is obtained by adding new feed each cycle in either step 1 or step 2; which process is better may be apparent in specific cases, but often will be determined by testing each possibility.

Example 1. Figure 8 shows process constructions for a system in which the doubly saturated points have $[A, B]$ coordinates as follows:

$$b(1) = [2.8, 24.2]$$

$$b(2) = [17.7, 15.0]$$

Crystal crops are assumed to be imperfectly separated, and will have the following coordinates:

$$\text{Crystal species A} = [35.0, 1.5]$$

$$\text{Crystal species B} = [1.0, 95.0]$$

The feed assumed for this example:

$$\mathbf{F} = [30.0, 45.0]$$

We consider the process in which new feed will be added in the path from operating point $b(2)$ to $b(1)$.

In the forward path from $b(1)$ to $b(2)$, liquid phase of composition $b(1)$ is evaporated at $T(2)$, corresponding to vector $b(1)-a$. This causes a crop of species **B** to crystallize, corresponding to vector $a-b(2)$.

The return path comprises adding an amount of new feed corresponding to some vector $b(2)-c$, diluting to d , and crystallizing a crop of species **A** at temperature $T(1)$ to return the mother liquor composition to point $b(1)$. The composition of point c can be determined by material balance since the amount of either solute added per cycle must equal that removed.

Material balance may be easily made as follows. Take 100 units of new feed as a basis:

- (1) The solutes in new feed \mathbf{F} are split ultimately into the solutes in crystal crop **A** plus those in crystal crop **B**. Substituting appropriately in Equation 6, it will be found that 1.27 units of component B end up as impurities in crystal crop **A**. This leaves, by difference, 43.73 units for crystal crop **B**.

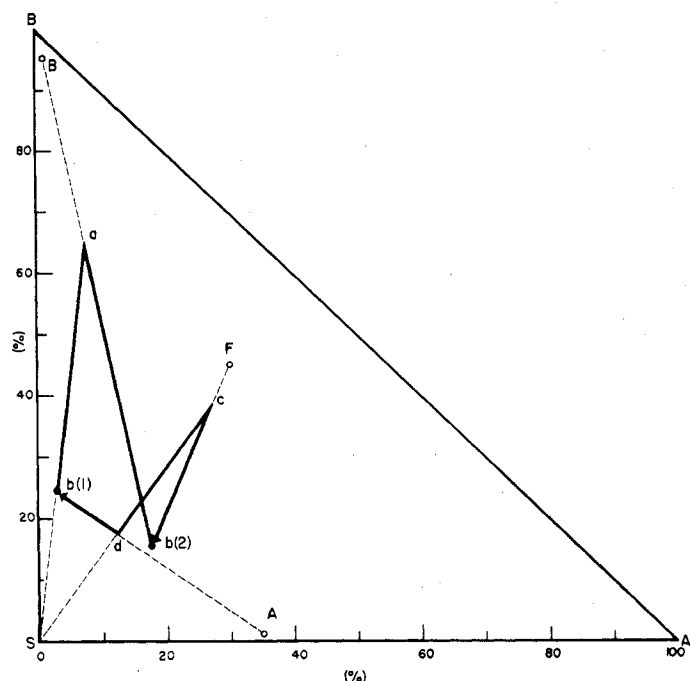


Figure 8. Type I process cycle

(2) In the path from $b(1)$ to $b(2)$, the solutes in liquor $b(1)$ are split into those in $b(2)$ plus those in crystal crop B . The amount of component B in crystal crop B is now known. Again, making use of the method of ratios, it will be found that liquor $b(2)$ must contain 4.33 units of component B . Summing B from B and $b(2)$ gives 48.06 units for liquor $b(1)$.

(3) From given compositions it is now easy to complete material balance calculations, including the amount of dilution or evaporation needed in each path. Composition of system point c is found by adding the components in new feed to those in liquor $b(2)$.

In the above example A is Na_2CO_3 , B is NaCl , and the temperatures are 0° and 30°C , respectively. The above exemplifies a standard process for separating the solutes of a three-component system.

Construction of new feed vector. The length of the new feed vector $b(2)-c$ in Figure 8 was found by making material balance calculation. It is sometimes useful, particularly in preliminary considerations of processes, to determine it by construction. This is done as follows: Project compositions of feed and crystal crops along dilution rays to the line of zero solvent (Figure 9) establishing points F' , A' , and B' . (Note that each dilution ray is the locus of points with constant A/B ratio. The procedure will be called *ratio projection*.)

If new feed is to be added to solution $b(2)$, construct any vector that represents taking the system from the A/B ratio of $b(1)$ to that of $b(2)$ by crystallizing B' . In Figure 9 it is $a'-b(2)$. Construct an A' ray through the tail of this vector and an F' ray through its head. The two rays will intersect at some point c' , and the true point c , representing system composition after addition

of new feed, will fall at the intersection of the dilution ray through c' and a line joining $b(2)$ and F .

Example 2—special leach cycle. In example 1 both operating points $b(1)$ and $b(2)$ were doubly saturated. In some important instances it is economical to accept less than the maximum crystal crop in each process cycle, and to choose an operating point saturated with only the crystallizing phase. Figure 9 shows the 80° and 20° isotherms for the system KCl , NaCl , H_2O . If liquor of composition $b(2)$ is cooled to 20°C , it will yield a liquor of composition a and a crop of pure KCl . Instead of evaporating solution a to reach doubly saturated point $b(1)$, point a is itself taken as the operating point. The crystal crop of KCl is separated, the temperature of solution a is raised to 80°C , and enough new feed is added to reach system point c . KCl is leached from the new feed, leaving NaCl as its residue, and regenerating solution $b(2)$.

The simple process triangle of Figure 10 corresponds to the five-vector cycle of Figure 9, with the two dilution ray vectors made null. This commercially important leach cycle requires no evaporation or dilution.

Type II Systems—Double Salts

The solubility chart of a system in which some double salt AB forms will appear as in Figure 11.

Solutions plotting along the isotherm $a-b$ will be in equilibrium with solids B , as may be indicated by tie lines back to composition B . Along $c-d$ they will be in equilibrium with solids A . However, along $b-c$ they will be in equilibrium with the double salt AB .

Subsidiary axes and systems. A dilution ray through solids point AB may be considered as an AB axis, as valid and meaningful as the A or B axis. That is, any composition plotting between the A and AB axes may be expressed just as well in terms of A and AB as it can in terms of A and B . For example, if A is Na_2SO_4 , B is K_2SO_4 , and AB is glaserite, $3 \text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$, the composition of a system might be expressed equally well as 50% K_2SO_4 and 10% Na_2SO_4 , or as 13.2% K_2SO_4 and 46.8% glaserite. Put another way, a glaserite vector and a K_2SO_4 vector form the basis for a vector space representing system compositions.

Therefore, the part of the diagram lying between $S-A$ and $S-AB$ represents a system A , AB , S . Since no further double salts are formed between A and AB , it may be considered a Type I system. Any system with a higher A/B ratio than that of double salt AB can, therefore, be fractionated into A and AB by Type I procedures.

Likewise, that part of the diagram bounded by the AB and B axis also represents a Type I system, AB , B , S , and can be separated into pure phases of AB and B .

These subsidiary systems will be called subsystems

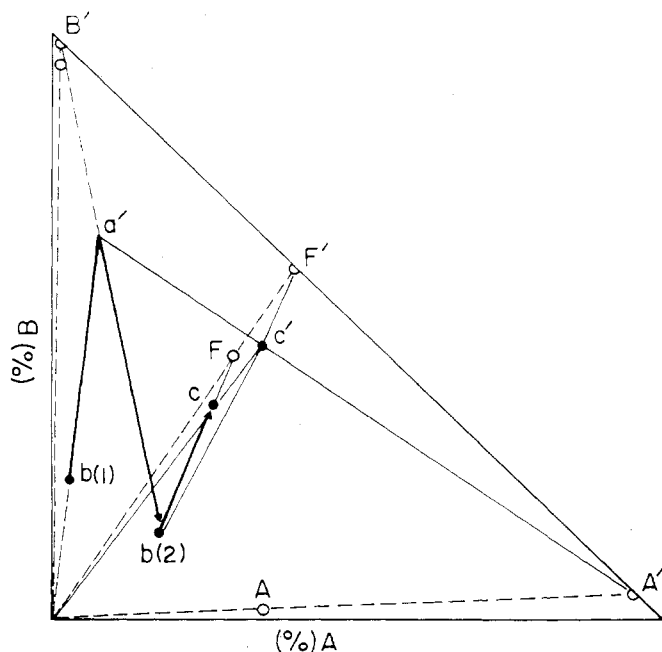


Figure 9. Construction for new feed vector

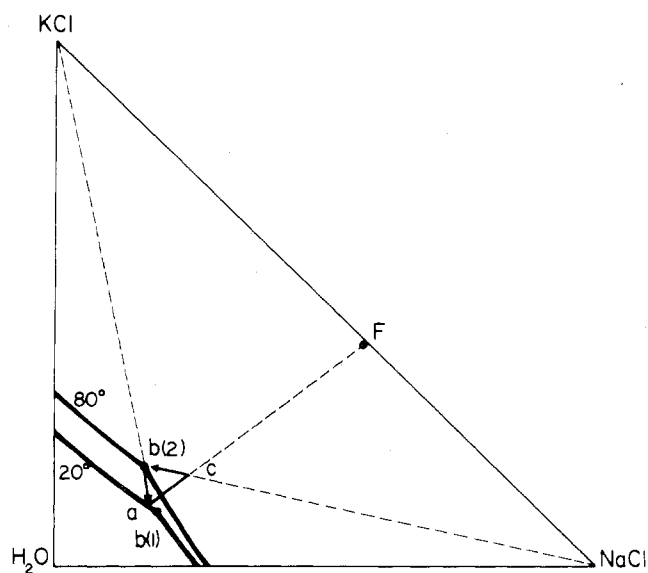


Figure 10. Modified Type I process cycle separation of KCl and NaCl

$A-AB$ and $AB-B$, the presence of S being understood in all cases.

C-level separation. What we need to find, then, is some way to break down the double salt so as to produce an A -enriched fraction lying well within the $A-AB$ subsystem, and a B -enriched residue lying as far as possible into the $AB-B$ subsystem. Once this is done, each fraction can be further processed by Type I procedures, as necessary, to recover some A , some B , and some AB that can be recycled. We will call such disproportioning of a double salt a "C-level separation."

Where the double-salt axis passes through the double-salt isotherm $b-c$, as in Figure 11, the double salt is said to be congruently soluble—it is in equilibrium with a solution having the same A/B ratio. This condition permits no C-level separation since a solution of AB , when evaporated, yields an AB ratio in both fractions.

In order to make a C-level separation, it is necessary to find a temperature or condition such that a solid phase of one of the components, such as B , is in equilibrium with a solution lying in the other subsystem $A-AB$.

Example—the system $MgSO_4$, K_2SO_4 , H_2O . The system $MgSO_4$, K_2SO_4 , H_2O is used to exemplify a Type II system, in part because it comprises hydrated solids and gives an example of their treatment.

Figure 12 is a three-dimensional picture of the system, in which temperature is added as a third variable and axis.

The phase diagram at $50^\circ C$ is shown in Figure 13. From $a(50)$ at composition $[0, 33.5]$ to $b(50)$ at $[4.74, 31.32]$, saturated solution is in equilibrium with $MgSO_4 \cdot 6 H_2O$, whose composition vector is $[0, 52.7]$. From $b(50)$ to $c(50)$ at $[23.25, 11.98]$, it is in equilibrium with

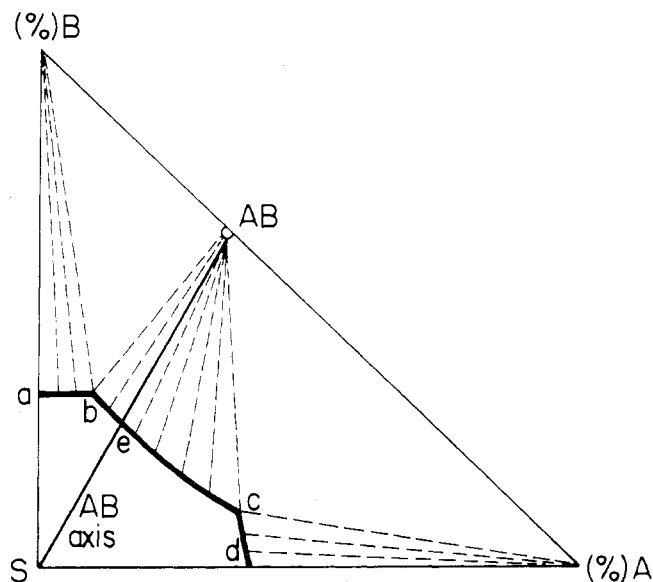


Figure 11. Typical solubility diagram—Type II

astrakanite, $Na_2SO_4 \cdot MgSO_4 \cdot 4 H_2O$, whose composition vector is $[42.5, 36.0]$. From $c(50)$ to $d(50)$ at $[31.7, 0]$, it is in equilibrium with Na_2SO_4 . No C-level split is possible at this temperature because astrakanite is congruently soluble.

The $25^\circ C$ isotherms are as shown, among others, in Figure 14. The magnesium sulfate solid phase has become $MgSO_4 \cdot 7 H_2O$; the sodium sulfate solid phase, $Na_2SO_4 \cdot 10 H_2O$. Astrakanite is still congruently