Algebraic Extrapolation of Tie Lines in Ternary Phase Diagrams

Sir:

Binary and ternary phase diagrams are being increasingly applied to pharmaceutical systems to represent the phase relationships of solid–liquid systems (1–3). Most ternary systems contain both solids and liquids. Schreinemakers developed an experimental procedure, called the method of wet residues (4), for determining the composition of solid phases; this method eliminates the necessity of removing all of the adhering mother liquor. It consists of preparing two or more ternary mixtures of known composition or of analyzing for the compositions of the corresponding liquid phases. The composition of the *wet* solids is also determined by analysis. The composition of the dry, pure solid phase is then determined by the point of convergence of the extrapolated tie lines, each passing through the composition of the liquid phase and/or the composition of the initial mixture, plus the composition of the wet solid.

The composition of the pure solid phase common to all systems can be determined by graphical extrapolation or, with higher accuracy, by algebraic extrapolation. An existing procedure for the algebraic extrapolation of tie lines useful in calculating the results for the method of wet residues is described. Its limitations are discussed and the procedure is extended to yield an explicit equation, which can be used for a general case and eliminates the necessity of making any assumptions regarding the composition of the solid phase.

According to the Hill and Ricci method (5), the amount of one of the three components in the solid phase must be known or assumed. For instance, in a system containing solids *A* and *B* plus water, the solid must be known to be a dihydrate or to be anhydrous. A simple proportion between the differences in the amounts of two components at the two known points, and the differences in the amounts of the same components at one of those points and at the composition of the solid phase, results in the composition of the solid phase (5). For instance, if a mixture made up of components *A* and *B* plus water, containing 80% of water and 6.5% of *A*, gives a solution containing 90% of water and 7% of *A*, one can calculate the content of *A* in the solid phase, p_A, provided the solid is anhydrous, by the following proportion:

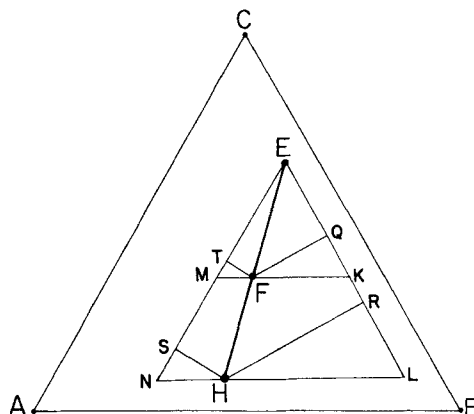$$\frac{(7 - 6.5 = 0.5)}{(90 - 80 = 10)} = \frac{x}{(90 - 0 = 90)} \qquad \text{(Eq. 1)}$$

Figure 1—*Tie line EFH in the ternary phase diagram of components* A, B, *and* C.

Hence, $x = 4.5\%$ and $p_A = 7 - 4.5 = 2.5\%$.

Assuming the solid to be anhydrous eliminates one concentration variable; the composition of the solid phase can be determined from a single tie line. The concordance of the results can be assessed by departure of the data from the assumed composition (5).

This procedure has the following shortcomings. It becomes cumbersome for higher solvates and for liquid–liquid systems. It does not cover the case of several converging tie lines, nor does it give an explicit equation for the representation of a single tie line (6). The advantage of using explicit equations for converging tie lines is the possibility of calculating their common intersection by the method of least squares, thereby minimizing the errors of chemical analysis. Since a set of tie lines based on experimental data seldom converges sharply on a single point, the applicability of statistical methods is a desirable feature.

Such an equation is derived, following the considerations of Hill and Ricci (5). In Fig. 1, consider the tie line *EFH* in the Gibbs triangle *ABC* (3, 4), where *E* represents the composition of the solution in equilibrium with a solid phase of composition represented by *H*, and *F* is made to represent either the composition of the original mixture or of the wet residue. The contents of the two components, *A* and *B*, usually expressed as weight percentages, are p_{A1} and p_{B1} at *E*, p_{A2} and p_{B2} at *F*, and p_A and p_B at *H*. It is desired to calculate p_A and p_B, knowing the other four *p* values.

Through point *E* are drawn *EKL* parallel to the side *BC*, and *EMN* parallel to the side *AC*, so that *MK* and *NL* are parallel to the third side *AB*. The line *FQ* is drawn perpendicular to *EL* and to *BC* and represents, therefore, $p_{A2} - p_{A1}$ according to the properties of the Gibbs ternary phase triangle (3, 4). Likewise, *HR* is perpendicular to *EL* and to *BC* and represents $p_A - p_{A1}$; *HS* and *FT* are drawn perpendicular to *EN* and to *AC* and represent $p_B - p_{B1}$ and $p_{B2} - p_{B1}$, respectively. The four triangles *FQK*, *HRL*, *NSH*, and *MTF* are similar because they have the same angles; one

is 90° and a second 60° according to the construction of Fig. 1, so the third angle is 30°. This results in the proportion

$$(p_A - p_{A1})/(p_{A2} - p_{A1}) = (p_B - p_{B1})/(p_{B2} - p_{B1}) \quad \text{(Eq. 2)}$$

Multiplying out and simplifying result in

$$p_A\,p_{B2} - p_{A1}\,p_{B2} - p_A\,p_{B1} - p_{A2}\,p_B + p_{A1}\,p_B +$$
$$p_{A2}\,p_{B1} = 0 \quad \text{(Eq. 3)}$$

This is identical with

$$\begin{vmatrix} p_A & p_B & 1 \\ p_{A1} & p_{B1} & 1 \\ p_{A2} & p_{B2} & 1 \end{vmatrix} = 0 \quad \text{(Eq. 4)}$$

This last expression is equivalent to those of another method of extrapolation (7), as it should be since both are solutions of the same problem. The present method has the advantage of being more direct. By applying Eq. 4 to two or more systems having convergent tie lines, the composition of the pure solid phase is obtained. If the data for several tie lines are available, the best fit for the composition corresponding to their common intersection can be calculated by least-squares analysis (8, 9). This minimizes the effect of random analytical errors.

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Compaction Effect on Flow Property Indexes for Powders

Sir:

Powder technologists are reluctant to suggest a single figure to describe the flow properties of a powder since it is recognized that many factors such as moisture,
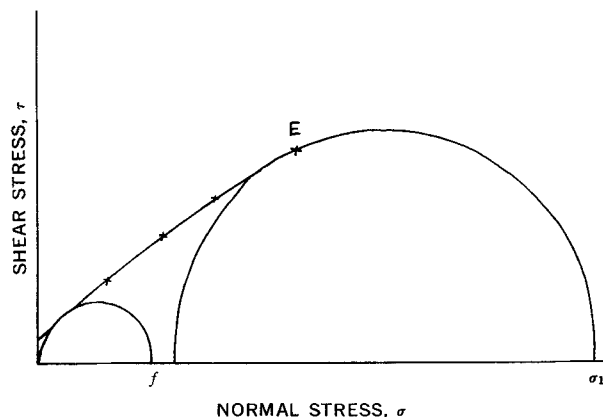

Figure 1—*Idealized Jenike yield locus.*

temperature, degradation, and time affect flow properties. Manufacturers, on the other hand, require a simple measure of the flow properties of their powders for process control—hence, the prevalent use of the much criticized angle of repose tests.

Two methods, both based on results obtained from a shear cell, have been suggested for characterizing powders with regard to their flow properties. The method of Jenike *et al.* (1) is called the flow factor, while that of Ashton *et al.* (2, 3) is termed the shear index.

Consider a yield locus, as shown in Fig. 1, which is obtained in the normal manner using a shear cell (1). Two Mhor circles are drawn, one passing through the origin and tangential to the locus and the other tangential to and passing through the end-point of the locus.

The basis of the Jenike flow factor, ff, is that the unconfined yield strength, f, of a powder is a function of the consolidating stress, σ_1, applied during the sample preparation. Small values of f in relation to the value of σ_1 will indicate a free-flowing material. The flow factor, ff, is taken as the ratio σ_1/f. It is found that values of ff generally range between 1 for highly cohesive powders and 10 for free-flowing powder.

If a family of yield loci are produced at a series of compaction levels and the values of f and σ_1 are measured for each locus, it is found that the flow factor usually increases with increasing compaction.

When the shear cell is used in conjunction with a tensile tester, the end-point of the locus on the negative portion of the normal stress axis (the tensile strength T) may be plotted. Thus the complete locus can be drawn as shown in Fig. 2. It was shown by Ashton *et al.* (2)
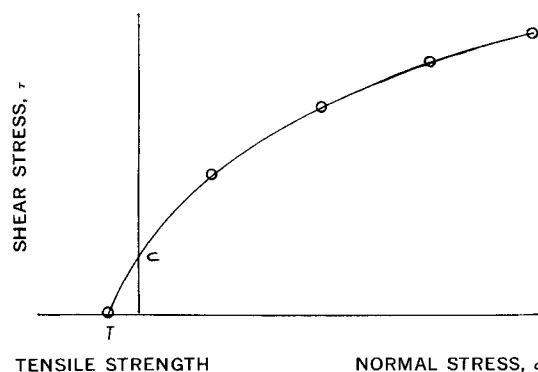

Figure 2—*Complete yield locus including tensile strength.*