A Mathematical Extrapolation for The Method of Wet Residues

HANS SCHOTT[1] University of Delaware, Newark, Del.

IN TERNARY SYSTEMS involving at least one solid and one liquid phase, the composition of the solid phase is often determined indirectly, in order to avoid separating the crystals and completely removing the adhering mother liquor from them. Extrapolation is made by Schreinemakers' method of wet residues (*3*), based on the following: The tie line joining the composition of the pure solid and of the saturated liquid in equilibrium with it is the locus of all intermediate compositions corresponding to varying amounts of solid and liquid phase. This includes the composition of the original mixture and of crystals wet with mother liquor. Needed are any two of the following three compositions: liquid phase, original mixture, and wet solid. A straight line drawn through a pair of points representing such compositions on a phase diagram is a segment of the tie line, and therefore passes through the composition of the pure solid. The lines drawn through several such pairs of composition, each corresponding to a different original mixture, have a common intersection at the composition of the pure solid phase.

This extrapolation is commonly made graphically. Algebraic extrapolation is less subjective, more accurate, and lends itself to the application of statistical methods which minimize errors.

MATHEMATICAL EXTRAPOLATION

In a ternary system of components *A*, *B*, and *C*, compositions are fully defined by two out of the three weight percentages p_A, p_B, and p_C, since they add up to 100. Hence, to simplify establishing the equations of the tie lines, the triangular diagram is converted to the Cartesian system of rectangular coordinates.

According to Gibbs (*2*), the composition of a ternary system is represented by an equilateral triangle. For any point inside an equilateral triangle, the sum of the perpendicular distances to the three sides is equal to the height of the triangle. If the height is set equal to 100, the distances equal the percentages of the three components in the composition represented by that point.

The composition represented by point *E* in the triangular system of Figure 1 is $p_A = EF$ and $p_B = EL = JK$; EJ is parallel and equal to LK, whence $\angle EJF = \angle KCJ = 60°$.

The coordinates of point *E* in the Cartesian system must be expressed in terms of p_A and p_B alone. The ordinate

$$y = EF = p_A \tag{1}$$

The abscissa

$$x = BF = BC - FJ - JC \tag{2}$$

Applying Pythagoras' theorem to the rectangular triangle AHB,

$$BC = 200/3^{1/2}$$

$$BC = 200/3^{1/2} \tag{3}$$

In the rectangular triangle *EJF*,

$$FJ = EF/\tan \angle\ EJF = p_A/3^{1/2} \tag{4}$$

In the rectangular triangle *KCJ*,

$$JC = JK/\sin \angle\ KCJ = 2p_B/3^{1/2} \tag{5}$$

Substituting Equations 3, 4, and 5 into 2 produces

$$x = (200 - p_A - 2p_B)/3^{1/2} \tag{6}$$

Equations 1 and 6 permit calculating the coordinates of a point in the Cartesian system. As a test, the mixture consisting of equal parts of *B* and *C* is represented by point *H*, for which $y = 0$ and $x = ½\ BC = 100/(3)^{1/2}$. Equations 1 and 6 give the correct values, $p_A = 0$ and $p_B = 50$. Equations 1 and 6 can also be derived for the Roozeboom triangle.

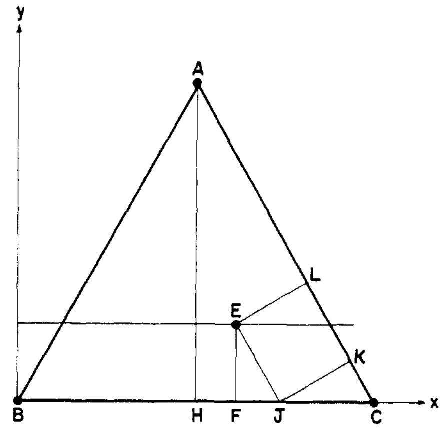

Figure 1. Triangular and rectangular system of coordinates

The following example illustrates the procedure. In a system of rectangular coordinates, the equation of the straight line passing through points (x, y), (x_1, y_1) and (x_2, y_2) is

$$\begin{vmatrix} x & y & 1 \\ x_1 & y_1 & 1 \\ x_2 & y_2 & 1 \end{vmatrix} = 0 \tag{7}$$

No subscript refers to the composition of the solid phase, subscript 1 designates the composition of the saturated liquid phase (determined by analysis) and subscript 2 designates the composition of the original mixture (calculated from the amounts of components weighed out). Among the pairs of compositions reported (*1*) for the system calcium chloride(*A*) – water(*B*) – dioxane(*C*) are:

	Composition			
	Liquid phase		Original mixture	
No.	p_A	p_B	p_A	p_B
3	43.9	52.4	44.9	41.4
6	39.1	49.8	41.8	38.5

Application of Equations 1 and 6 gives

No.	x_1	y_1	x_2	y_2
3	29.618	43.900	41.742	44.900
6	35.392	39.100	46.881	41.800

The equations of the two tie lines, calculated by means of Equation 7, are for No. 3

$$-x + 12.124\,y - 502.64 = 0 \tag{8}$$

and for No. 6

$$x - 4.255\,y + 130.99 = 0 \tag{9}$$

Simultaneous solution of Equations 8 and 9 gives $x = 69.985$ and $y = 47.229$. From Equations 1 and 6 one obtains $p_A = 47.23$ and $p_B = 15.77$. Hence, the pure solid phase consists of 47.23% $CaCl_2$, 15.77% H_2O and 37.00% $C_4H_8O_2$, or on a mole basis, 1.00 $CaCl_2$, 2.06 H_2O and 0.99 $C_4H_8O_2$. It is $CaCl_2 \cdot 2H_2O \cdot C_4H_8O_2$.

LITERATURE CITED

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[1] Present address, Film Division, Olin Mathieson Chemical Corp., New Haven 4, Conn.