CHAPTER 19

Mixture Ingredients as Predictor Variables

19.1 MIXTURE EXPERIMENTS: EXPERIMENTAL SPACES

Response surface experiments often involve mixtures of ingredients. For example, fuels can consist of a mixture of petroleum and various additives; fish patties may contain several types of fish; a fruit juice drink may consist of a mixture of orange, pineapple, and grapefruit juices; or a regional wine may be blended from several grape varieties. This adds a restriction to the problem, often of type

$$x_1 + x_2 + \cdots + x_q = 1, \tag{19.1.1}$$

where the predictor variables are proportions, $0 \le x_i \le 1$, $i = 1, 2, \ldots, q$. Note that a more general restriction such as $c_1t_1 + c_2t_2 + \cdots + c_qt_q = 1$, where the c_i are specified constants, can be converted to (19.1.1) by recoding $c_it_i = x_i$ for $i = 1, 2, \ldots, q$. The restriction displayed above means that the complete x-space is not available for collecting data.

Two Ingredients

Consider the simplest case, $q = 2$, for which $x_1 + x_2 = 1$. This defines (see Figure 19.1) a straight line in the (x_1, x_2) space. Because $0 \le x_1, x_2 \le 1$, however, only that part of the line between and including the points (0, 1) and (1, 0) defines the appropriate mixture space. All points on this segment take the form $(x_1, 1 - x_1)$ or $(1 - x_2, x_2)$. If x_1 is the proportion of gin in a mixed drink and x_2 is the proportion of tonic water, all possible gin and tonic mixtures will lie on the line segment described. (One might question whether drinks with no gin, or drinks with only gin, can properly be called "mixtures," but it is conventional to do so, in this context.)

Three Ingredients

When $x_1 + x_2 + x_3 = 1$, the mixture space is defined by a portion of a plane containing the three extreme mixture points $(x_1, x_2, x_3) = (1, 0, 0)$, $(0, 1, 0)$, and $(0, 0, 1)$ and such that $0 \le x_i \le 1$. It is thus a two-dimensional equilateral triangle with the extreme points as the vertices, as depicted in Figure 19.2. Note that each side of the triangle is a two-ingredient subspace, with the third ingredient set equal to zero. Compare the (x_2, x_3) axes part of Figure 19.2 with Figure 19.1, for example. The Dietzgen Corporation

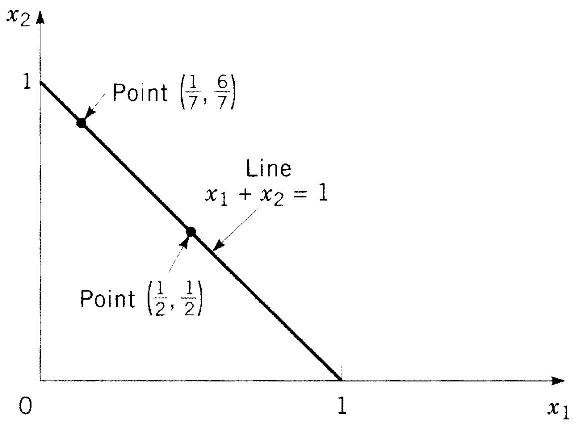

Figure 19.1. A one-dimensional experimental mixture space $x_1 + x_2 = 1$ embedded in the two-dimensional (x_1, x_2) space. Only the region for which $0 \leq x_i \leq 1$ is valid, as shown.

manufactures a triangular coordinate (TC) graph paper (No. 340-TC) that has three sets of lines—one set parallel to each of the three sides of the triangle. The depiction of Figure 19.3*a* illustrates one of these three sets of lines, and Figure 19.3*b* illustrates how the intersection of any two lines from different sets defines a point in the mixture space. Naturally $x_3 = 1 - x_1 - x_2$, so we do not actually need the third set of lines (which *does* appear on Dietzgen 340-TC paper, however) to fully define the point.

Four Ingredients

The original four-dimensional space cannot be drawn but the mixture space is now a regular (equal-sided) tetrahedron, shown in Figure 19.4*a*. Any point (x_1, x_2, x_3, x_4) in or on the boundaries of the tetrahedron is such that $x_1 + x_2 + x_3 + x_4 = 1$. Each triangular face is defined by $x_i = 0$ for $i = 1, 2, 3,$ and 4. It is easy to construct a tetrahedron in three dimensions for yourself, as indicated in Figure

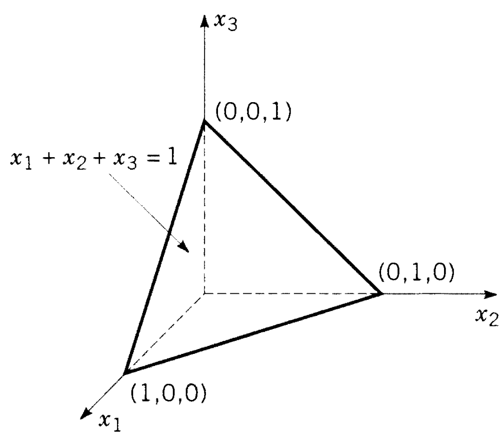

Figure 19.2. A two-dimensional experimental mixture space $x_1 + x_2 + x_3 = 1$ embedded in the three-dimensional (x_1, x_2, x_3) space. Only the region for which $0 \leq x_i \leq 1$ is valid, as shown.

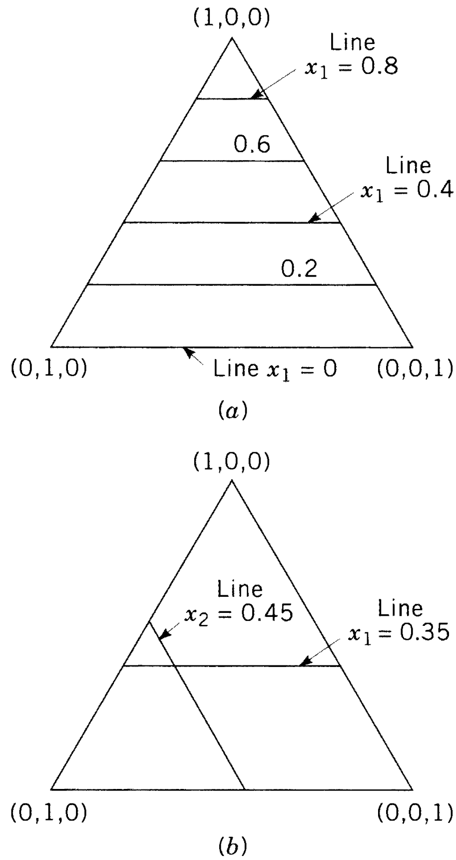

Figure 19.3. (*a*) Parallel coordinate lines $x_1 = 0, 0.2, 0.4, 0.6$, and 0.8 in the mixture space $x_1 + x_2 + x_3 = 1$. (*b*) The point (0.35, 0.45, 0.20) defined by the intersection of the two coordinate lines $x_1 = 0.35$ and $x_2 = 0.45$. Note that $x_3 = 1 - x_1 - x_2 = 0.20$.

19.4*b*. First, draw and then cut out an equilateral triangle indicated by the 1's. Next, join up, in pairs, the midpoints 2, 3, and 4 of the sides to produce four equal-sized triangles as shown. Use the triangle 234 as the base and fold along the lines 23, 24, and 34. Bring the three points marked 1, 1, and 1 together into one point 1. Tape the two sides 12 together where they meet and do the same for 13 and 14. The point 1 is defined by (1, 0, 0, 0), point 2 by (0, 1, 0, 0), and so on. The 234 face is defined by $x_1 = 0$ and similarly for the other faces. One can also imagine the tetrahedron built up in triangular slices $x_1 = c$, where $c = 0$ on the base 234 and where c increases to 1 at the vertex marked 1. This slicing can be imagined relative to any of the x_i dimensions, of course. For example, Figure 19.4*c* shows slices at about $x_1 = 0.15$ and $x_1 = 0.85$.

Five or More Ingredients

For five ingredients, the best we can do pictorially is to imagine a series of tetrahedra of diminishing size. The largest would be defined by $x_5 = 0$, and successive ones would be $x_5 = c$, where c increases from 0 to 1. When $x_5 = 1$ we have the point (0, 0, 0, 0, 1), which is the limiting case of these tetrahedra.

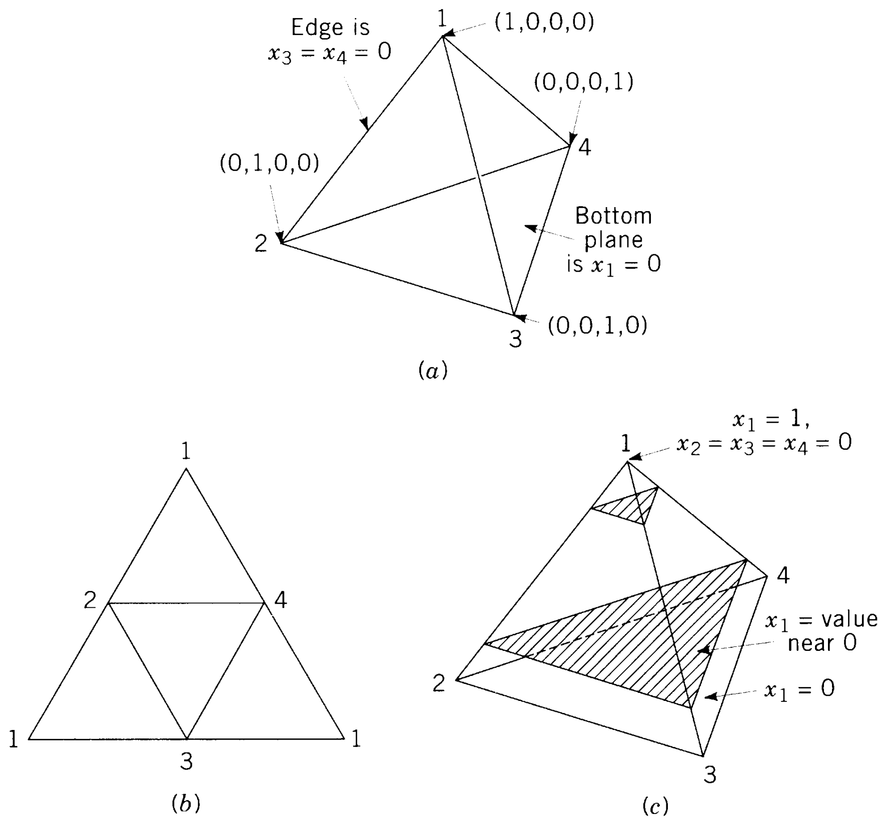

Figure 19.4. (*a*) The mixture space for four ingredients is an equal-sided tetrahedron (pyramid). (*b*) Construction of an equal-sided tetrahedron model. (*c*) Slices of four-ingredient mixture space for which x_1 is nearer 0 or nearer 1.

19.2. MODELS FOR MIXTURE EXPERIMENTS

We discuss models in detail for $q = 3$ ingredients; the pattern of models for general q will then become easy to understand.

Three Ingredients, First-Order Model

It is quickly obvious that the usual polynomial response surface models no longer can be used. Consider, for example, the planar model function

$$\beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3. \tag{19.2.1}$$

The $\mathbf{X}$ matrix consists of four columns $[\mathbf{1}, \mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3]$ For each line of this matrix, however, the mixture restriction requires that $1 = x_1 + x_2 + x_3$ so that a linear relationship holds between the four columns of $\mathbf{X}$. Although we have a three-dimensional x-space, the space of the experimental domain is only two-dimensional; see Figure 19.2. Thus, in the usual least squares regression fit formulation $\mathbf{b} = (\mathbf{X}'\mathbf{X})^{-1}\mathbf{X}'\mathbf{Y}$, where $\mathbf{X}$ is the matrix of observed x-data, $\mathbf{Y}$ is the vector of responses, and $\mathbf{b}$ is the vector of estimates of the parameter vector $\boldsymbol{\beta}$ in the model $\mathbf{Y} = \mathbf{X}\boldsymbol{\beta} + \boldsymbol{\epsilon}$, the matrix $\mathbf{X}'\mathbf{X}$ is singular and its inverse does not exist. This difficulty can be overcome in either of two (essentially the same but mechanically different) ways:

1. Use the restriction (19.1.1) to transform the model symmetrically into *canonical form.*
2. Transform the q original x-coordinates to $q - 1$ new z-coordinates. (This is regarded as somewhat tedious to do, especially for $k \geq 4$.) See Appendix 19A.

Canonical Form

Method 1 was pioneered by Scheffé (1958, 1963) and is now illustrated for $q = 3$. By rewriting

$$\beta_0 = \beta_0(x_1 + x_2 + x_3), \tag{19.2.2}$$

using the fact that $x_1 + x_2 + x_3 = 1$, we can rewrite (19.2.1) as

$$(\beta_0 + \beta_1)x_1 + (\beta_0 + \beta_2)x_2 + (\beta_0 + \beta_3)x_3 \tag{19.2.3}$$

or

$$\alpha_1 x_1 + \alpha_2 x_2 + \alpha_3 x_3, \tag{19.2.4}$$

where $\alpha_i = \beta_0 + \beta_i$. This canonical form is simply a no-intercept plane. One way of looking at this is that, since (19.2.1) is overparameterized because of the mixture restriction (19.1.1), the least squares problem has an infinity of solutions. One of these solutions is the one for which we choose $\beta_0 = 0$ in (19.2.1), which gives us a model of form (19.2.4). This type of model is appealing because of its symmetry in the x's. Less appealing, but just as valid, would be any model obtained by deletion of any one term in (19.2.1). There are also other valid choices. All valid choices give the same fitted values.

q Ingredients, First-Order Model

The extension to q ingredients leads to the canonical form model function (we revert now to using β's)

$$\eta = \beta_1 x_1 + \beta_2 x_2 + \cdots + \beta_q x_q, \tag{19.2.5}$$

and of course we then fit $y = \eta + \epsilon$ by least squares.

Example: The Hald Data

The 13 observations of Table 15.1 (or see Appendix 15A) are used to fit the model

$$Y = \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \epsilon \tag{19.2.6}$$

by least squares. The X's here are percentages, not proportions, we recall. Moreover, the data are not "perfect" mixture data in the sense that the X's do not add to the same total *exactly*. The fitted equation is

$$\hat{Y} = 2.1930X_1 + 1.1533X_2 + 0.7585X_3 + 0.4863X_4 \tag{19.2.7}$$

and the corresponding (no intercept, remember) analysis of variance table is:

Source	df	SS	MS	F
b_1, b_2, b_3, b_4	4	121,035	30,259	5176
Residual	9	53	6	
Total	13	121,088		

Obviously such a model explains nearly all the variation in the data. We do not calculate an R^2 value because there is no intercept in the model and so the R^2 statistic is not defined. We could, of course, drop any one $\beta_i X_i$ term and replace it by β_0. *If the data were "perfect" mixture data*, that is, if the X's added *exactly* to the same total, any of the resulting four fitted models and the model (19.2.7) would all provide the same $\hat{Y}$ predictions. As we have already observed in Appendix 15A, there is some slight variation in the R^2 values for the four three-X models with intercepts and there will be variation in the fitted values also.

Test for Overall Regression

Note that in fitting the model function (19.2.5), it makes little sense to test that $\beta_1 = \beta_2 = \cdots = \beta_q = 0$, leading to the reduced model $Y = \epsilon$. The appropriate null hypothesis is $H_0: \beta_1 = \beta_2 = \cdots = \beta_q$ $(= \beta_0$, say) whereupon the reduced model would be simply $Y = \beta_0 + \epsilon$ due to (19.1.1). We would have

$$\mathrm{SS}(H_0) = \mathrm{SS}(b_1, b_2, \ldots, b_q) - n\overline{Y}^2 \qquad (19.2.8)$$

and would perform the usual test comparing $\mathrm{SS}(H_0)/q$ with the residual mean square from the full model.

This will not work perfectly for the Hald data, but approximately we can say that $\mathrm{SS}(H_0) = 121{,}035 - 118{,}372 = 2663$ with 3 df, leading to an approximate F-value of $(2663/3)/6 = 148$, indicating the need for more than an overall mean value.

As we have seen in Chapter 15, a three-parameter model containing an intercept and X_1 and X_2 terms appears to be satisfactory for representing the data. The no-intercept model (19.2.7) provides an alternative possibility with four terms instead of three, and this alternative would provide the same fitted values as all the three-X equations if the data were "perfect" mixture data in the sense described above.

Three Ingredients, Second-Order Model

The usual second-order model

$$g(\mathbf{x}, \boldsymbol{\beta}) = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 \qquad (19.2.9)$$

produces a singular $\mathbf{X}'\mathbf{X}$ matrix. As before, we replace β_0 with $\beta_0 x_1 + \beta_0 x_2 + \beta_0 x_3$. In addition, because $x_1 = 1 - x_2 - x_3$, we have $x_1^2 = x_1 - x_1 x_2 - x_1 x_3$, and similarly for x_2^2 and x_3^2. Substituting these four relationships in (19.2.9), gathering like terms, and renaming coefficients gives

$$h(\mathbf{x}, \boldsymbol{\alpha}) = \alpha_1 x_1 + \alpha_2 x_2 + \alpha_3 x_3 + \alpha_{12} x_1 x_2 + \alpha_{13} x_1 x_3 + \alpha_{23} x_2 x_3. \qquad (19.2.10)$$

This is called the canonical form of the three-ingredient second-order model.

q Ingredients, Second-Order Model

The general second-order canonical form model is clearly (reverting to β's)

$$\beta_1 x_1 + \beta_2 x_2 + \cdots + \beta_q x_q + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \cdots + \beta_{q-1,q} x_{q-1} x_q. \quad (19.2.11)$$

A null hypothesis of no quadratic effects returns us to the reduced model (19.2.5) with first-order terms only.

Example: The Hald Data

Adding second-order terms does nothing much for us with these data since the residual SS from the first-order model is already tiny (53). Several near dependencies are created, not surprisingly. The addition of only the $x_2 x_3$ term reduces the residual SS to zero (to the nearest integer). This fit looks perhaps better than the reality. When we check where the data points are in the mixture space, we see the following. Apart from one point where $X_1 = 21$, all the data have $X_1 < 11$ so that they are squashed into a thin set of planes between $X_1 = 0$ and $X_1 = 11$. Moreover, eight of the X_3 values are small, less than or equal to 9. The remaining five points have $X_1 = 1, 2$, or 3 (near 0) and fan out somewhat away from the $X_3 = 0$ wall of the tetrahedron. In short, most of the points cover a rather restricted region of the space and provide information adequate for fitting only a few parameters. So a fit with only three or four parameters is not unreasonable. Moreover, extrapolation into the rest of the mixture space is likely to be quite dangerous. An approximate plot of the data is shown in Figure 19.5.

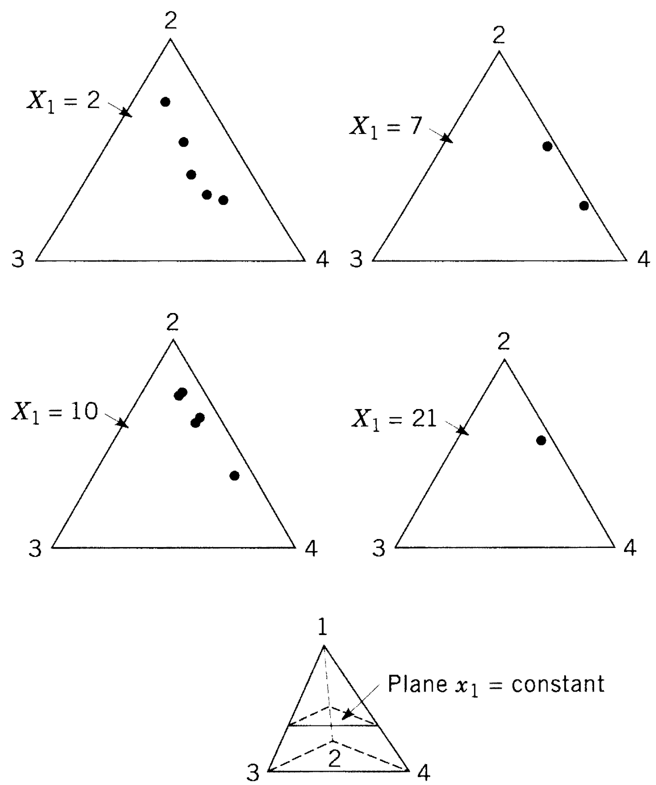

Figure 19.5. An approximate sectional plot of the Hald data onto the planes $X_1 = 2, 7, 10$, and 21.

Because we have plotted the planes $X_1 = 2, 7, 10$, and 21 only, some points are slightly above or below the planes shown. Also, we recall that the X-values for each point do not add perfectly to 100% anyway. Nevertheless, the diagram does clearly indicate the restricted nature of the data.

Third-Order Canonical Model Form

Third-order models of two main types are sometimes used. They also possess canonical forms. For $q = 4$, for example, we can fit the *general cubic* model function

$$\begin{aligned} h(\mathbf{x}, \boldsymbol{\beta}) = {} & \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 \\ & + \beta_{14} x_1 x_4 + \beta_{23} x_2 x_3 + \beta_{24} x_2 x_4 + \beta_{34} x_3 x_4 \\ & + \alpha_{12} x_1 x_2 (x_1 - x_2) + \alpha_{13} x_1 x_3 (x_1 - x_3) + \alpha_{14} x_1 x_4 (x_1 - x_4) \qquad (19.2.12) \\ & + \alpha_{23} x_2 x_3 (x_2 - x_3) + \alpha_{24} x_2 x_4 (x_2 - x_4) + \alpha_{34} x_3 x_4 (x_3 - x_4) \\ & + \beta_{123} x_1 x_2 x_3 + \beta_{124} x_1 x_2 x_4 + \beta_{134} x_1 x_3 x_4 + \beta_{234} x_2 x_3 x_4 . \end{aligned}$$

For the *special cubic*, the six α_{ij} terms are deleted from (19.2.12). Note that when $q = 3$ [so that all terms containing x_4 are deleted in (19.2.12)], the general cubic contains four terms more than the quadratic while the special cubic contains only one more, namely, $\beta_{123} x_1 x_2 x_3$.

Scheffé Designs

While the usual response surface designs can be employed for mixture experiments, special designs linked to the canonical forms were suggested by Scheffé. These designs typically consist of combinations of symmetrical point sets. Some examples are given below. For more detail, and for a comprehensive treatment of the mixtures area in general, see Cornell (1990).

Design 1. The {3, 2} lattice. (Three factors and six points, which use the levels $\frac{0}{2}$, $\frac{1}{2}$, and $\frac{2}{2}$.) (1, 0, 0), (0, 1, 0), (0, 0, 1), (0.5, 0.5, 0), (0.5, 0, 0.5), and (0, 0.5, 0.5). Sometimes, the centroid $(\frac{1}{3}, \frac{1}{3}, \frac{1}{3})$ is added, also.

Design 2. The {3, 3} lattice. (Three factors and ten points, which use the levels $\frac{0}{3}$, $\frac{1}{3}$, $\frac{2}{3}$, and $\frac{3}{3}$.) (1, 0, 0), (0, 1, 0), (0, 0, 1), $(\frac{2}{3}, \frac{1}{3}, 0)$, $(\frac{1}{3}, \frac{2}{3}, 0)$, $(\frac{2}{3}, 0, \frac{1}{3})$, $(\frac{1}{3}, 0, \frac{2}{3})$, $(0, \frac{2}{3}, \frac{1}{3})$, $(0, \frac{1}{3}, \frac{2}{3})$, and $(\frac{1}{3}, \frac{1}{3}, \frac{1}{3})$. The design *includes* the centroid.

Design 3. The {4, 2} lattice. Ten points: (1, 0, 0, 0), (0, 1, 0, 0), (0, 0, 1, 0), (0, 0, 0, 1), (0.5, 0.5, 0, 0)(0.5, 0, 0.5, 0), (0.5, 0, 0, 0.5)(0, 0.5, 0.5, 0), (0, 0.5, 0, 0.5), (0, 0, 0.5, 0.5). Sometimes the centroid (0.25, 0.25, 0.25, 0.25) is added also.

Design 4. The {4, 3} lattice. Twenty points: (1, 0, 0, 0), (0, 1, 0, 0), (0, 0, 1, 0), (0, 0, 0, 1), $(\frac{2}{3}, \frac{1}{3}, 0, 0)$, $(\frac{1}{3}, \frac{2}{3}, 0, 0)$, $(\frac{2}{3}, 0, \frac{1}{3}, 0)$, $(\frac{1}{3}, 0, \frac{2}{3}, 0)$, $(\frac{2}{3}, 0, 0, \frac{1}{3})$, $(\frac{1}{3}, 0, 0, \frac{2}{3})$, $(0, \frac{2}{3}, \frac{1}{3}, 0)$, $(0, \frac{1}{3}, \frac{2}{3}, 0)$, $(0, \frac{2}{3}, 0, \frac{1}{3})$, $(0, \frac{1}{3}, 0, \frac{2}{3})$, $(0, 0, \frac{2}{3}, \frac{1}{3})$, $(0, 0, \frac{1}{3}, \frac{2}{3})$, $(\frac{1}{3}, \frac{1}{3}, \frac{1}{3}, 0)$, $(\frac{1}{3}, \frac{1}{3}, 0, \frac{1}{3})$, $(\frac{1}{3}, 0, \frac{1}{3}, \frac{1}{3})$, $(0, \frac{1}{3}, \frac{1}{3}, \frac{1}{3})$. Sometimes the centroid (0.25, 0.25, 0.25, 0.25) is added also.

19.3. MIXTURE EXPERIMENTS IN RESTRICTED REGIONS

In many mixture experiments, exploration of the entire mixture domain (e.g., for $q = 3$, this is the triangle in Figure 19.2) is not feasible or perhaps undesirable. A common type of restriction is that each ingredient has a lower bound, such as $x_1 \geq$

a_1, $x_2 \geq a_2$, $x_3 \geq a_3$, as in Figure 19.6*a*. Obviously this produces a restricted space of the same shape as the original mixture space, so that any design considerations can be translated to the smaller space exactly. To do this one simply transforms into new *pseudo-coordinates*

$$x_1' = \frac{x_1 - a_1}{1 - A}, \qquad x_2' = \frac{x_2 - a_2}{1 - A}, \qquad x_3' = \frac{x_3 - a_3}{1 - A}, \tag{19.3.1}$$

where $A = a_1 + a_2 + a_3 < 1$. The inner triangle of Figure 19.6 is then defined by the sides $x_1' = 0$ (corresponding to $x_1 = a_1$), $x_2' = 0$ ($x_2 = a_2$), and $x_3' = 0$ ($x_3 = a_3$). Moreover, $x_1' + x_2' + x_3' = 1$. The extension to more ingredients is obvious.

When upper *and* lower bounds are specified, for example, $b_1 \geq x_1 \geq a_1$ and so on, the domain shape is different from the original one, as shown in Figure 19.6*b*. One simple way of choosing some experimental points is to select all or some of the extreme vertices of the domain in an optimum way via some selected criterion. The extreme vertices in our example are the black dots in Figure 19.6*b*. The criterion used might be any of those used in experimental design situations that do not involve mixture ingredients (e.g., *D*-optimality). Other points, centroids of the boundaries, for example, can be added to the set of points under consideration for the design. In dimensions higher than three, the boundaries will be of several kinds. In addition to one-dimensional edges, as in the $q = 3$ case, there will also be two-dimensional polyhedra

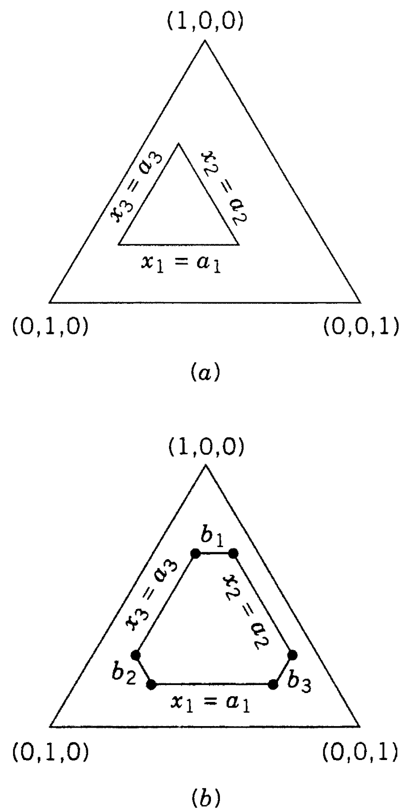

Figure 19.6. Restrictions in the $q = 3$ mixture space. (This space is pulled from Figure 19.2 and shown in two dimensions.) (*a*) Each ingredient must exceed a lower bound. (*b*) Each ingredient has an upper and a lower bound.

TABLE 19.1. Propellent Data

Mixture Point (i)	x_1	x_2	x_3	Y_i
1	0.40	0.40	0.20	2.35
2	0.20	0.60	0.20	2.45
3	0.20	0.40	0.40	2.65
4	0.30	0.50	0.20	2.40
5	0.30	0.40	0.30	2.75
6	0.20	0.50	0.30	2.95
7	0.267	0.467	0.267	3.00
8	0.333	0.433	0.233	2.69
9	0.233	0.533	0.233	2.77
10	0.233	0.433	0.333	2.98

faces, and so on, depending on the number of ingredients. For more details, consult Cornell (1990).

19.4. EXAMPLE 1

[*Source:* Kurotori, 1966. The original paper had a different emphasis to that given in our adaptation. It presented a basic set of data, to which the model was fitted, plus some checkpoints to test lack of fit. It also illustrated the use of *pseudo-components;* a restricted region of same shape as the mixture region was recoded as in (19.3.1) so that the new (pseudo-component) coordinates mimicked the original mixture space. Here, we use all the data together to fit a second-order mixture model in canonical form in the original mixture proportion coordinates and find a best region of operation in the restricted space directly.]

In making a certain type of propellant, three mixture ingredients have their proportions restricted as follows:

$$\begin{aligned} \text{Binder } (x_1) &\geq 0.2, \\ \text{Oxidizer } (x_2) &\geq 0.4, \\ \text{Fuel } (x_3) &\geq 0.2. \end{aligned} \tag{19.4.1}$$

We thus have the situation of Figure 19.6*a* with

$$a_1 = 0.2, \qquad a_2 = 0.4, \qquad a_3 = 0.2. \tag{19.4.2}$$

The data are given in Table 19.1. The original responses, values of modulus of elasticity, have been divided by 1000. It is desired to find, within the permissible subspace, mixtures that will provide response values of at least 3 and that will also involve the minimum possible amount of x_1. The basic design chosen was an "augmented {3, 2} simplex lattice" (see Design 1 at the end of Section 19.2). When translated into the restricted space, it consists of the six points numbered 1 to 6 in Table 19.1, augmented by the centroid point numbered 7. The points numbered 8, 9, and 10 were additional checkpoints, and these will also be included in our regression fit. The responses observed are shown in the Y column of Table 19.1.

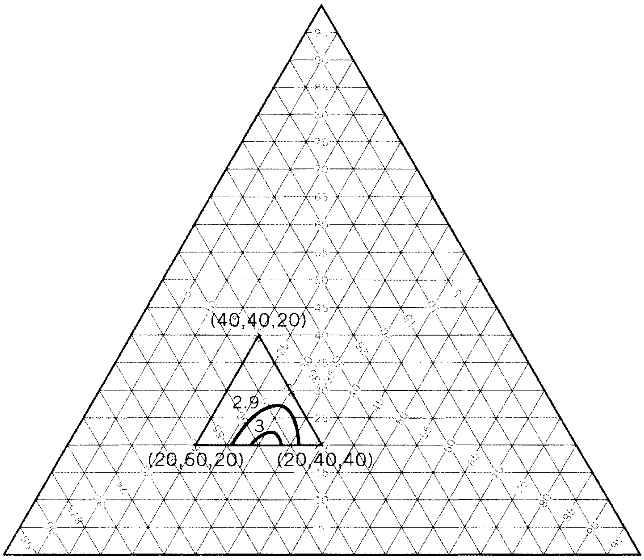

Figure 19.7. Estimated response contours within the restricted region.

The model we select for this problem is the second-order canonical polynomial

$$Y = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \epsilon. \qquad (19.4.3)$$

The fitted least squares equation, with standard errors of coefficients in parentheses, is

$$\begin{array}{cccccc} \hat{Y} = -2.756x_1 & - \; 3.352x_2 & - \; 17.288x_3 & + \; 9.38x_1x_2 & + \; 34.76x_1x_3 & + \; 49.49x_2x_3. \\ (4.1) & (2.0) & (4.1) & (10.7) & (10.7) & (10.7) \end{array}$$

It is an excellent fit; $s = 0.1$. Figure 19.7 shows the restricted region and the $\hat{Y} = 2.9$ and 3.0 contours. Desirable readings are at the lower boundary around the point $x_1 = 0.20$, $x_2 = 0.49$, and $x_3 = 0.31$, approximately. (A confirmatory run later showed that the response level predicted *could* actually be attained at this location.)

19.5. EXAMPLE 2

(*Source:* Draper et al., 1993.) The data in Table 19.2 come from an investigation of four bread flours that were combined in proportions denoted by x_1, x_2, x_3, and x_4 and were baked into loaves. The response values are specific volumes (mL/100 g), and higher specific volumes are more desirable. Four blocks of experiments were performed. Blocking is a normal procedure at Spillers Milling Limited (then a member of the Dalgety Group of companies) where the experiment was performed, to reduce the possible disturbances from within-day time effects. It was anticipated, as a result of previous studies, that these baking-session effects would alter the mean level of the response but would not interact with the x's. It was further anticipated that a second-order model function of form

$$\begin{aligned} h(\mathbf{x}, \boldsymbol{\beta}) = {} & \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 \\ & + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{14} x_1 x_4 + \beta_{23} x_2 x_3 + \beta_{24} x_2 x_4 + \beta_{34} x_3 x_4 \end{aligned} \qquad (19.5.1)$$

would be satisfactory. (All these assumptions were to be checked, of course.) The model to be fitted was thus chosen as

TABLE 19.2. Orthogonally Blocked Design and Response Values ($b = 0.25$, $d = 0.75$)

Blocks 1 and 3				Responses from Block		Blocks 2 and 4				Responses from Block	
x_1	x_2	x_3	x_4	1	3	x_1	x_2	x_3	x_4	2	4
0	b	0	d	403	381	0	d	0	b	423	404
b	0	d	0	425	422	b	0	d	0	417	425
0	d	0	b	442	412	0	b	0	d	398	391
d	0	b	0	433	413	d	0	b	0	407	426
0	d	b	0	445	398	0	0	b	d	388	362
b	0	0	d	435	412	b	d	0	0	435	427
0	0	d	b	385	371	0	b	d	0	379	390
d	b	0	0	425	428	d	0	0	b	406	411
0.25	0.25	0.25	0.25	433	393	0.25	0.25	0.25	0.25	439	409

$$Y = z_1 h(\mathbf{x}, \boldsymbol{\beta}) + \gamma z_2 + \delta z_3 + \omega z_4 + \epsilon, \tag{19.5.2}$$

where the z's are dummy variables to separate blocks, allocated as in Table 19.3. (The design used is, in fact, orthogonally blocked and nearly D-optimal although these points do not specifically concern us here.)

An initial fit to the model (19.5.2) showed nonsignificant t-values for the coefficients of x_2x_3, x_2x_4, and x_3x_4. An *extra sum of squares* test, for all three as a unit, confirmed that it was reasonable to omit all three from the model. The resulting fitted model was

$$\begin{aligned}\hat{Y} = {} & \underset{(11.1)}{397.6x_1} + \underset{(6.8)}{444.5x_2} + \underset{(7.5)}{389.4x_3} + \underset{(6.8)}{395.8x_4} \\ & + \underset{(41.7)}{107.8x_1x_2} + \underset{(41.6)}{217.9x_1x_3} + \underset{(41.7)}{169.7x_1x_4} \\ & - \underset{(5.2)}{14.9z_2} - \underset{(5.2)}{21.8z_3} - \underset{(5.2)}{20.1z_4}.\end{aligned} \tag{19.5.3}$$

Standard errors are shown in parentheses below their respective coefficients. An examination of residuals did not reveal any alarming characteristics. Figure 19.8 provides the $x_1 = 0$, 0.25, and 0.75 cross sections of the $\hat{Y}$ contours when $z_2 = z_3 = z_4 = 0$ in the four-dimensional mixture space. We see that these cross sections show planes, but that the actual contours curve as the value of x_1 is changed. The maximum estimated response within the mixture space is 453.1 at the edge point (0.283, 0.717, 0, 0), which is close to the corner point (0.25, 0.75, 0, 0) shown in Figure 19.8*b*. Note that the responses actually observed at this corner point (453, 427) were lower than the 453.0 predicted there when $z_2 = z_3 = z_4 = 0$ because they were depressed by the block

TABLE 19.3. Dummy Variables for Four Blocks

Baking Session	z_1	z_2	z_3	z_4
1	1	0	0	0
2	1	1	0	0
3	1	0	1	0
4	1	0	0	1

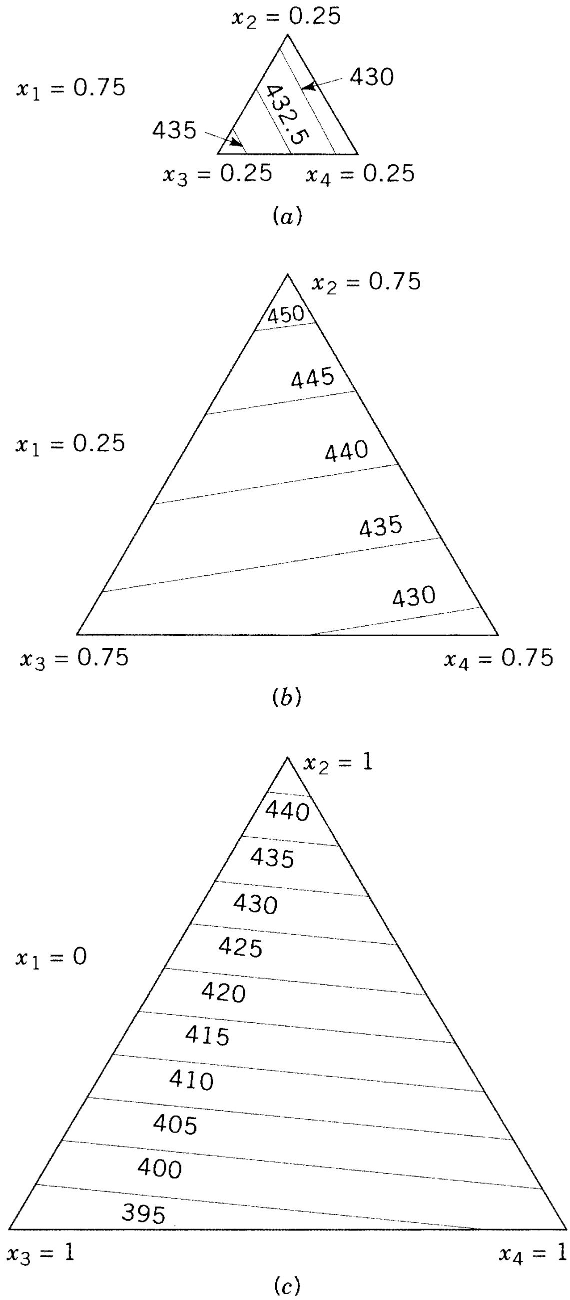

Figure 19.8. Contours of the fitted surface (19.5.3) when $z_2 = z_3 = z_4 = 0$. Sections are shown at (*a*) $x_1 = 0.75$, (*b*) $x_1 = 0.25$, and (*c*) $x_1 = 0$.

effects for blocks 2 and 4, estimated as -14.9 and -20.1, respectively. Allowing for blocks in the analysis enables us to make proper response comparisons.

The design used in this example consists mostly of blends of only two ingredients. Some experiments use single ingredients and these are not really mixtures at all. Whether such runs are adequate or need to be supplemented by three- and fourcomponent blends is a question that needs to be carefully considered before any experiment is conducted.

References

Cornell (1990), Draper et al. (1993), Kurotori (1966), Scheffé (1958, 1963).

APPENDIX 19A. TRANSFORMING q MIXTURE VARIABLES TO $q - 1$ WORKING VARIABLES

We first illustrate the transformation from basic variables x to working variables z for the case $q = 3$. In this case we write

$$
\begin{aligned}
z_1 &= -\frac{\sqrt{3}}{2}x_1 + \frac{\sqrt{3}}{2}x_2, \\
z_2 &= -\tfrac{1}{2}x_1 - \tfrac{1}{2}x_2 + x_3, \\
z_3 &= x_1 + x_2 + x_3 = 1,
\end{aligned}
$$

or $\mathbf{z} = \mathbf{Tx}$, where

$$
\mathbf{z} = \begin{bmatrix} z_1 \\ z_2 \\ z_3 \end{bmatrix}, \qquad \mathbf{T} = \begin{bmatrix} -\dfrac{\sqrt{3}}{2} & \dfrac{\sqrt{3}}{2} & 0 \\ -\frac{1}{2} & -\frac{1}{2} & 1 \\ 1 & 1 & 1 \end{bmatrix}, \qquad \mathbf{x} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix}.
$$

The *inverse* transformation, which takes z to x, is $\mathbf{x} = \mathbf{T}^{-1}\mathbf{z}$, where

$$
\mathbf{T}^{-1} = \frac{1}{3}\begin{bmatrix} -\sqrt{3} & -1 & 1 \\ \sqrt{3} & -1 & 1 \\ 0 & 2 & 1 \end{bmatrix}
$$

so that the z to x reverse transformation for $q = 3$ takes the form

$$
\begin{aligned}
x_1 &= -\frac{\sqrt{3}}{3}z_1 - \tfrac{1}{3}z_2 + \tfrac{1}{3}z_3, \\
x_2 &= \frac{\sqrt{3}}{3}z_1 - \tfrac{1}{3}z_2 + \tfrac{1}{3}z_3, \\
x_3 &= \tfrac{2}{3}z_2 + \tfrac{1}{3}z_3.
\end{aligned}
$$

Figure 19A.1 illustrates how the corner points and the center point of our triangular region when $q = 3$ are described both in (x_1, x_2, x_3) coordinates and in (z_1, z_2) coordinates. The (z_1, z_2) axes are also shown. Note that, since $z_3 = 1$ always, we do not need to give it. The z_3 axis would be drawn from the $z_1 = z_2 = 0$ point out perpendicularly from the plane of the paper. [The z-origin, given by $z_1 = z_2 = z_3 = 0$, lies *below* the plane of the paper by a distance of one unit. Since $z_3 = 1$ always on the mixture space, we can work from the $(z_1, z_2) = (0, 0)$ origin in the $z_3 = 1$ plane in practice.]

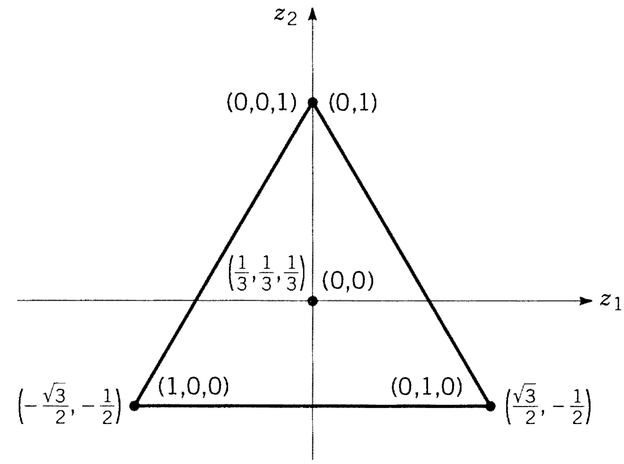

Figure 19A.1. Some points of the simplex region for $q = 3$ in both (x_1, x_2, x_3) and (z_1, z_2) notation.

General q

For general q we can still write $\mathbf{z} = \mathbf{Tx}$ and $\mathbf{x} = \mathbf{T}^{-1}\mathbf{z}$ but now

$$\mathbf{z} = \begin{bmatrix} z_1 \\ z_2 \\ \vdots \\ z_q \end{bmatrix}, \qquad \mathbf{x} = \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_q \end{bmatrix},$$

$$\mathbf{T} = \begin{bmatrix} -a & a & 0 & 0 & 0 & \cdots & 0 \\ -b & -b & 2b & 0 & 0 & \cdots & 0 \\ -c & -c & -c & 3c & 0 & \cdots & 0 \\ -d & -d & -d & -d & 4d & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & & \vdots \\ -t & -t & -t & -t & -t & \cdots & (q-1)t \\ 1 & 1 & 1 & 1 & 1 & \cdots & 1 \end{bmatrix}.$$

The values of $a, b, c, \ldots, t$ can be chosen as follows. The vertices of the simplex region are given by $(x_1, x_2, x_3, x_4, \ldots, x_q) = (1, 0, 0, 0, \ldots, 0)$, $(0, 1, 0, 0, \ldots, 0)$, $(0, 0, 1, 0, \ldots, 0), \ldots, (0, 0, 0, 0, \ldots, 1)$. These translate into z-points, which have coordinates that are the columns of $\mathbf{T}$. For example,

$$\begin{aligned} \mathbf{x}' &= (1, 0, 0, 0, \ldots, 0, 0) \rightarrow \mathbf{z}' = (-a, -b, -c, -d, \ldots, -t, 1), \\ &\vdots \\ \mathbf{x}' &= (0, 0, 0, 0, \ldots, 0, 1) \rightarrow \mathbf{z}' = (0, 0, \ldots, (q-1)t, 1). \end{aligned}$$

Suppose we choose the scale factors $a, b, c, \ldots, t$ so that, in the z-space, all points are one unit away from the point $(0, 0, \ldots, 0, 1)$, which will be our origin in the space of the factors $(z_1, z_2, \ldots, z_{q-1})$ since $x_q = 1$ always. Then the sum of squares of the first $(q - 1)$ elements in every column of $\mathbf{T}$ must be equal to 1. Thus

$$
\begin{aligned}
a^2 + b^2 + c^2 + d^2 + e^2 + \cdots + t^2 &= 1 \\
4b^2 + c^2 + d^2 + e^2 + \cdots + t^2 &= 1 \\
9c^2 + d^2 + e^2 + \cdots + t^2 &= 1 \\
16d^2 + e^2 + \cdots + t^2 &= 1 \\
\cdots & \\
(q-1)^2 t^2 &= 1.
\end{aligned}
$$

From these equations it follows that

$$a^2 = 3b^2, 2b^2 = 4c^2, 3c^2 = 5d^2, 4d^2 = 6e^2, \ldots, (q-2)s^2 = qt^2, \qquad t^2 = 1/(q-1)^2,$$

which implies that

$$2a^2 = 6b^2 = 12c^2 = 20d^2 = \cdots = (q-1)(q-2)s^2 = q(q-1)t^2 = q/(q-1).$$

This is precisely what we would obtain if we set the sum of squares of the elements of each of the first $(q-1)$ *rows* of $\mathbf{T}$ equal to $q/(q-1)$. This last, then, is the easiest way to choose the scale factors in $\mathbf{T}$ and it sets all the transformed simplex points the same distance, 1, from the new origin in the $(q-1)$-dimensional space of $z_1, z_2, \ldots, z_{q-1}$.

Example: $q = 3$. Here $2a^2 = 6b^2 = \frac{3}{2}$, so that $a = \sqrt{3}/2$, $b = \frac{1}{2}$, as given earlier.

Example: $q = 4$. Here $2a^2 = 6b^2 = 12c^2 = \frac{4}{3}$, so that $a = \sqrt{\frac{2}{3}}$, $b = \sqrt{2}/3$, $c = \frac{1}{3}$.

Example: $q = 5$. Here $2a^2 = 6b^2 = 12c^2 = 20d^2 = \frac{5}{4}$, so that $a = \sqrt{\frac{5}{8}}$, $b = \sqrt{\frac{5}{24}}$, $c = \sqrt{\frac{5}{48}}$, $d = \sqrt{\frac{5}{80}}$.

The general inverse transformation from z back to x is given by $\mathbf{x} = \mathbf{T}^{-1}\mathbf{z}$, where

$$
\mathbf{T}^{-1} = \frac{q-1}{q}
\begin{bmatrix}
-a & -b & -c & -d & \cdots & -t & \dfrac{1}{q-1} \\
a & -b & -c & -d & \cdots & -t & \dfrac{1}{q-1} \\
0 & 2b & -c & -d & \cdots & -t & \dfrac{1}{q-1} \\
0 & 0 & 3c & -d & \cdots & -t & \dfrac{1}{q-1} \\
0 & 0 & 0 & 4d & \cdots & -t & \dfrac{1}{q-1} \\
\vdots & \vdots & \vdots & & \vdots & \vdots & \\
0 & 0 & 0 & 0 & \cdots & (q-1)t & \dfrac{1}{q-1}
\end{bmatrix}.
$$

Comment. The presentation can be made somewhat simpler by taking the z-origin to be the center of the simplex, in other words choosing the point $(z_1, z_2, \ldots, z_q) = (0, 0, \ldots, 0)$ to be the center of the simplex instead of the point $(z_1, z_2, \ldots, z_{q-1}, z_q) = (0, 0, \ldots, 0, 1)$, which we *have* chosen. Then $\mathbf{T}$ can be chosen to be an orthogonal matrix so that $\mathbf{T}^{-1} = \mathbf{T}'$, the transpose of $\mathbf{T}$. The above, of course, comes close to this, except for scale factors and this is why $\mathbf{T}^{-1}$ is so easy to write down, above. The variation of **T** given simply keeps the situation a little closer to the practical mixture problem in holding $z_q = 1$, the mixture total.

EXERCISES FOR CHAPTER 19

A. The fit of a second-order model to some mixture data resulted in the fitted equation $\hat{Y} = 5x_1 + 6x_2 + 7x_3 + 3x_1x_2 + x_1x_3 + 2x_2x_3$. Substitute for the z-coordinates in Appendix 19A, and find the resulting equation in terms of z_1 and z_2. (Set $z_3 = 1$.)

B. Provide the appropriate transformation matrix for transforming four mixture variables to three "working" variables. Hence convert the points (0, 1, 0, 0), $(\frac{1}{2}, \frac{1}{2}, 0, 0)$, $(\frac{1}{3}, \frac{1}{3}, \frac{1}{3}, 0)$ and $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ to the new coordinates.

C. Four mixture ingredients are restricted to the space $0.10 \leq x_1 \leq 0.80$, $0.25 \leq x_2 \leq 0.45$, $0.20 \leq x_3 \leq 0.40$, $0.15 \leq x_4 \leq 0.55$. Find the extreme vertices of the restricted space, the face centroids, and the overall centroid.

D. Fit the quadratic model $Y = \beta_1x_1 + \beta_2x_2 + \beta_3x_3 + \beta_{12}x_1x_2 + \beta_{13}x_1x_3 + \beta_{23}x_2x_3 + \epsilon$ to the data below. Predict the response at the centroid $(\frac{1}{3}, \frac{1}{3}, \frac{1}{3})$. Plot the contours on triangular graph paper.

x_1	x_2	x_3	Y
1	0	0	40.9
0	1	0	25.5
0	0	1	28.6
0.5	0.5	0	31.1
0.5	0	0.5	24.9
0	0.5	0.5	29.1
0.2	0.6	0.2	27.0
0.3	0.5	0.2	28.4

E. Plot on triangular graph paper (e.g., Dietzgen 340-TC) these mixtures of three ingredients (x_1, x_2, x_3): (1, 0, 0), (0, 1, 0), (0, 0, 1), $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, \frac{1}{2})$, $(0, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{3}, \frac{1}{3}, \frac{1}{3})$.

F. Scheffé's *simplex lattice* design type uses $(m + 1)$ equally spaced levels of each mixture ingredient. (For example, if $m = 2$, the levels are $0, \frac{1}{2}, 1$.) Suppose we have q ingredients and we write down all $(m + 1)$ combinations of ingredients. Are they all suitable design points? Try this for $m = 2$, $q = 3$ and see why the answer is no. How many points *are* in the design in general?

G. Scheffé's *simplex centroid* type design consists of all vertices of the mixture space, plus all centroids (averages) of two or more of these points. Show that for $q = 3$ ingredients we get the points given in Exercise E.

H. How many regression coefficients are there in the second-order mixture model for $q =$ 3 ingredients? What does that mean if (a) Scheffé's simplex lattice design is used or (b) Scheffé's simplex centroid design is used.

I. A number of examples of the analysis of mixture data are exhibited and discussed in "Mixture experiment approaches: examples, discussion, and recommendations," by G. F. Piepel and J. A. Cornell, *Journal of Quality Technology,* **26**, 1995, No. 3, 177–196. Also see "A catalog of mixture experiment examples," by G. F. Piepel and J. A. Cornell, Report BN-SA-3298 (Revision 4), available from G. F. Piepel, Battelle, Pacific Northwest Laboratories, Richland, WA.