

## COMPUTER MODEL FOR BATTERY PASTE CALCULATIONS

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### Introduction

Paste mixes are formulated from various bases of knowledge and experience in the industry that take into account many parameters such as:

- type and nature of oxide
- free-lead content of oxide
- design and type of mixing equipment
- mix polarity (*i.e.*, for negative or positive plates)
- intended use of battery plates, *e.g.*, automotive, stationary, motive power.
- optimisation of various performance factors, *e.g.* active material utilisation at slow discharge rates, high-rate discharge voltage, climatic use-zone.

It is not the intention of this paper to address all of these parameters as most are proprietary or variable, but rather to reveal physicochemical guidelines, or limits, that should be observed in the formulation or subsequent processing of paste. This can best be understood and illustrated by the use of a computer model.

With the exception of various minor additives, battery paste mixes are compounded from:

- leady oxide
- water
- dilute sulphuric acid.

These three constituents can be regarded as derived from the more fundamental chemical phases:

- H<sub>2</sub>O, phase A
- PbO, phase B
- SO<sub>3</sub>, phase C.

As such, the composition of a paste mix and the composition of the paste in a plate up to the end of the curing process can be mathematically and graphically represented on triangular graph paper [1]. The properties of this paper are such that (Fig. 1):

(i) the triangular graph is equilateral and is sub-divided into equi-spaced similar triangles;

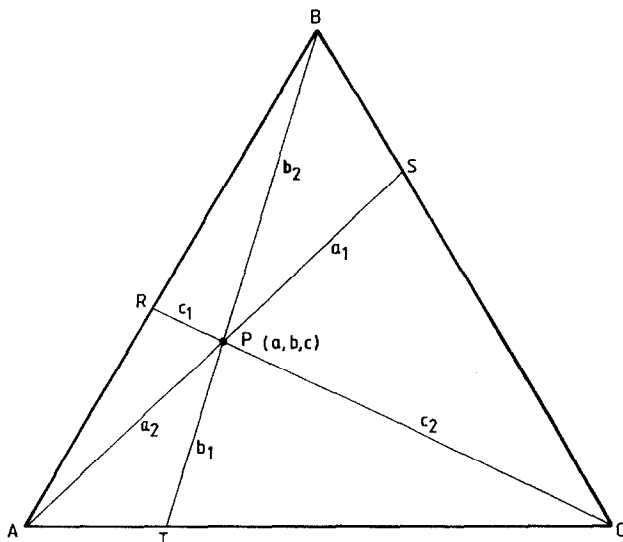


Fig. 1. Ternary diagram for three phases A, B, C.  $a = a_1/(a_1 + a_2)$ ;  $b = b_1/(b_1 + b_2)$ ;  $c = c_1/(c_1 + c_2)$ ;  $a + b + c = 1$ .

(ii) the fractional or the percentage amount of a phase, say A, in a mixture represented by a point P is equal to the ratio of the perpendicular distance of the point P to the opposite line BC ( $a_1$ ) and the perpendicular distance between A and its opposite side BC ( $a_1 + a_2$ ).

(iii) the sum of the three phases for any point is equal to 1 or 100%, depending on the chosen convention; in this model, the former notation has been chosen; thus, if the coordinates of any point P are  $a$ ,  $b$ ,  $c$ , then  $a + b + c = 1$ .

It is worth noting from the outset those mixtures that are represented by points falling on the boundary lines of the triangle ABC. Thus, using Fig. 2;

(i) line A-B represents suspensions, slurries and pastes consisting of water and lead oxide;

(ii) line A-C represents all strengths of sulphuric acid, including oleum and  $\text{SO}_3$ ;

(iii) line B-C represents mixtures of lead oxide, basic and non-basic lead sulphates and  $\text{SO}_3$  gas; all these species are in the dry state.

### Compositional changes during paste mixing

Initially, the mixture starts at point B(0,1,0), *i.e.*, lead oxide (see Fig. 2). With water addition, a slurry is produced, whence the composition changes to point  $P_1(a_1, b_1, 0)$ . When the acid addition is made to the slurry (using dilute sulphuric acid: sp.gr. = 1.4, typically),  $\text{SO}_3$  is being added simul-

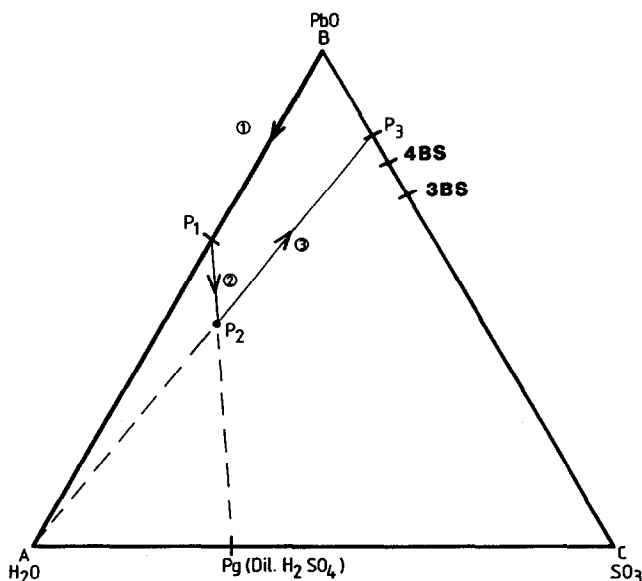


Fig. 2. Model of phase relations in processing of lead/acid battery pastes. Pathway  $B \rightarrow P_1 \rightarrow P_2 \rightarrow P_3$ : ① PbO and  $H_2O$  addition; ② acid addition; ③ curing and drying. Note, no free lead in starting oxide.

taneously with the dilution water of the acid and the water arising from the reaction:



At the end of acid addition, the composition is now represented by the point  $P_2 (a_2, b_2, c_2)$ . The following should be noted:

- (i) no allowance is made for water evaporation;
- (ii) during acid addition, the composition moves along the line joining the point  $P_1$  to the point  $P_g$  on the line AC;  $P_g$  represents the composition of the acid used, having an sp.gr. =  $g$ ; in other words,  $P_1$ ,  $P_2$  and  $P_g$  are co-linear;
- (iii) in both the model and the following sections, the free-lead content of the oxide has not been taken into account; free lead oxidation will be considered later as a refinement to the model.

### Compositional changes during skin-drying/plate-curing

Within the restrictions of note (iii) immediately above, the effects of skin drying and curing in terms of nominal composition are merely to reduce the water content of the paste to zero. Hence, the composition of the dry plate is represented as shown in Fig. 3, by the point  $P_3 (0, b_3, c_3)$  on the line BC. It should be noted that the points A,  $P_2$ ,  $P_3$  are co-linear.

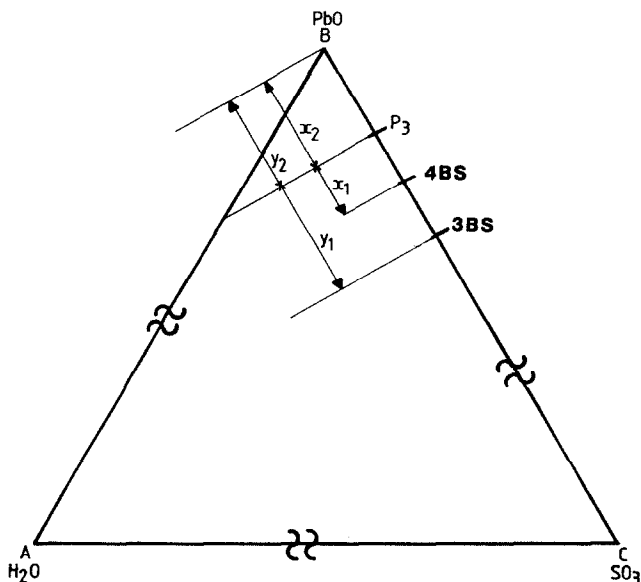


Fig. 3. Model of plate drying/curing (point  $P_3$ ) to give 3BS or 4BS.

The composition of the principal basic lead sulphate compounds, namely, tetrabasic ( $4\text{PbO} \cdot \text{PbSO}_4 = 4\text{BS}$ ) and tribasic ( $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O} = 3\text{BS}$ ) lead sulphate, that are of major importance in plate making are also represented by points on the line BC, *i.e.*,

$$4\text{BS} = (0, 0.933, 0.067) \quad (2)$$

$$3\text{BS} = (0, 0.918, 0.082) \quad (3)$$

Thus, if the coordinates of  $P_3$  are compared with the above, it can be ascertained whether the nominal composition of  $P_3$  is:

- (i) on the 'oxide' side of 4BS and therefore on the oxide side of 3BS;
- (ii) between 3BS and 4BS;
- (iii) beyond 3BS, *i.e.*, towards monobasic lead sulphate ( $\text{PbO} \cdot \text{PbSO}_4 = 1\text{BS}$ ). In the computer model, these relationships are measured and displayed by the variables  $X_3$  and  $X_4$ . A negative value of these parameters indicates  $P_3$  is on the  $\text{SO}_3$  side of the phase considered.

### Effect of including free lead

To simplify the inclusion of free lead in the model, the following additional assumptions have been made. First, it is assumed that oxidation of free lead does not take place during either water or acid addition. Second, the points  $P_1$  and  $P_2$  (Fig. 4) are most expeditiously calculated by using the weight  $W_1$  for  $P_1$  and the weight  $W_2$  for  $P_2$ , where:

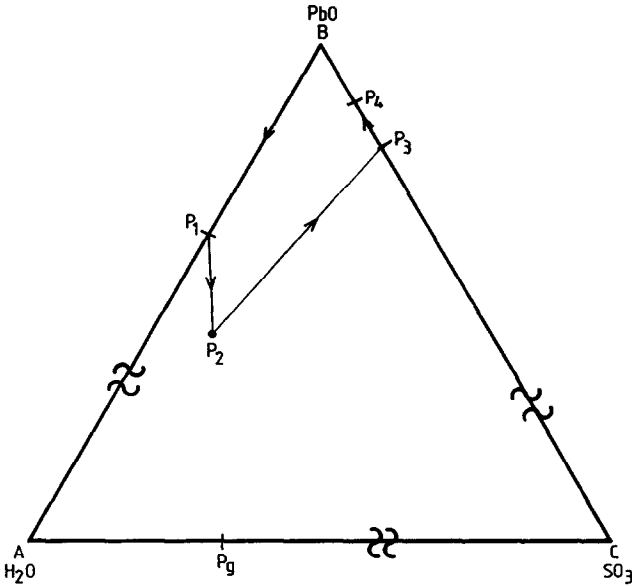


Fig. 4. Model of phase relations in preparation of lead/acid battery pastes as in Fig. 2 but including free-lead oxidation after paste formulation, *i.e.*, pathway  $P_3 \rightarrow P_4$ .

$$W_2 = W_1(100 - f)/100 \quad (4)$$

where  $f$  is the percentage of free lead in the starting oxide. The 'oxide' weight is  $W_1$  while the PbO weight is  $W_2$  and takes into account the percentage of free lead. During plate drying and curing, when free-lead oxidation does take place, the model can be used and the results interpreted as water loss and PbO generation occurring sequentially or, more realistically, these processes occurring simultaneously.

#### Compositional changes during plate curing: incorporating free-lead oxidation

Four points  $P_1, P_2, P_3, P_4$  representing sequential compositions are calculated (Fig. 4). The points correspond to the following paste-processing stages:

- $P_1$  — water addition, reduced amount of PbO as before (Fig. 2)
- $P_2$  — acid addition
- $P_3$  — plate drying from  $P_2$  as before (Fig. 2)
- $P_4$  — free-lead oxidation moving  $P_3$  up the line BC towards the PbO end-point, B.

Thus, the process pathway is  $B \rightarrow P_1 \rightarrow P_2 \rightarrow P_3 \rightarrow P_4$ .

Figure 5 represents the situation when free lead is included in the paste formulation so that there is simultaneous drying and oxidation of free lead

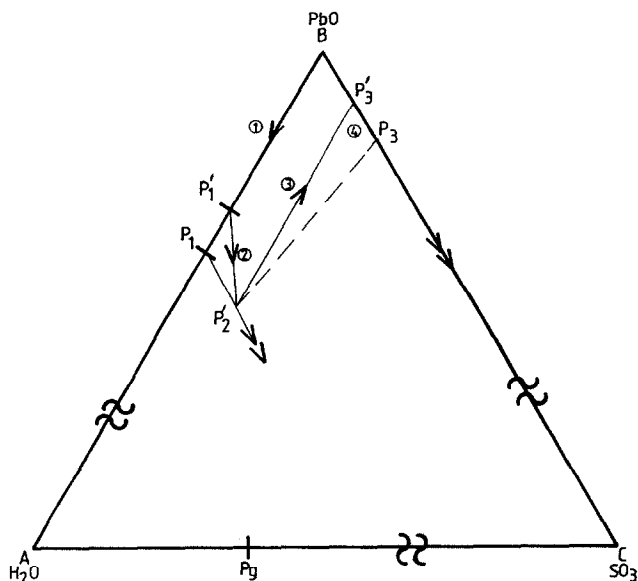


Fig. 5. Model of phase relations in preparation of lead/acid battery pastes as in Fig. 2 but including free lead in formulation. Pathway  $P_1' \rightarrow P_2' \rightarrow P_3'$  represents simultaneous drying and free-lead oxidation. Pathway  $P_1 \rightarrow P_2 \rightarrow P_3 \rightarrow P_3'$  represents sequential drying and free-lead oxidation.

during the curing stage. The process pathway is now  $B \rightarrow P_1' \rightarrow P_2' \rightarrow P_3'$ . By comparison, the pathway for sequential oxidation is  $B \rightarrow P_1 \rightarrow P_2 \rightarrow P_3 \rightarrow P_3'$ . The relative rate of water loss *versus* lead oxidation determines the practical pathway, which will be intermediate between the simultaneous and sequential routes.

### Process pathway limitations

When water is added to oxide, there is a maximum amount beyond which the mixture becomes 'too wet'. This water limit is basically established by the properties of the oxide, but when found, it can be represented on the phase diagram by a line  $W_L-W_L'$  that is parallel to the line BC (see Fig. 6).

It is a well known fact that the presence of monobasic lead sulphate, or indeed lead sulphate itself, is highly undesirable in paste mixes — either in a localised or on an overall compositional basis. It follows, therefore, that an acid limit line  $A_L-A_L'$ , joining 3BS to A can be established (Fig. 6). For the purpose of discussion, the composition of 3BS has been set as this limit, *i.e.*, any other point nearer to the  $SO_3$  phase is considered to be undesirable. The intersection of line  $A_L-A_L'$  with  $W_L-W_L'$  has been labelled  $P_{WAL}$  (Fig. 6).

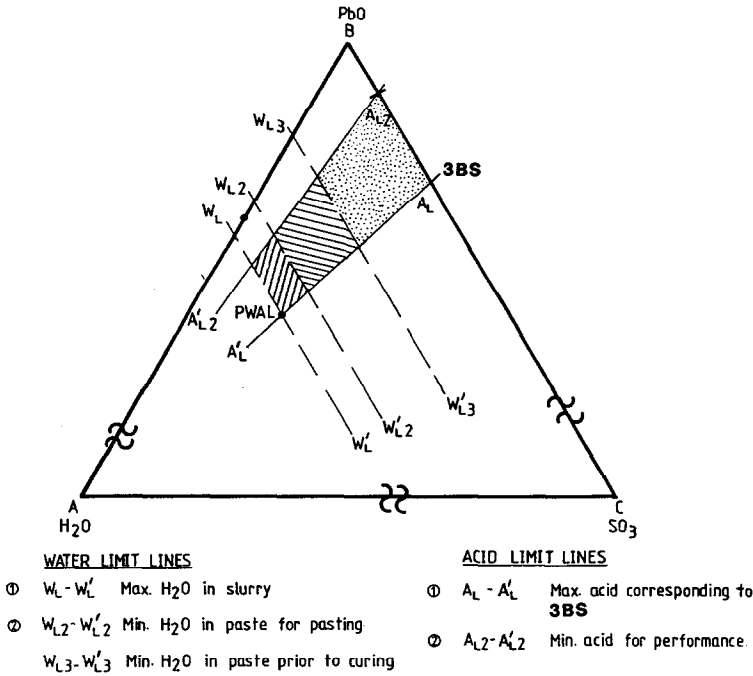


Fig. 6. Process pathway limitations.

By constructing phase diagrams that either include (Fig. 5) or exclude (Fig. 2) the presence of free lead in the starting oxide, a comparison can be made that reveals whether the expected paste-mixing variables will cause permanent or transient undesirable compositions and properties.

### Computer model

The calculations required to determine the  $(a, b, c)$  coordinates of the required points were performed on an IBM compatible computer using the proprietary software package TK! Solver<sup>®</sup>. These equations and a typical model printout are shown in Tables 1 - 4.

To display these results in graphical form, a secondary model again using TK! Solver<sup>®</sup>, as well as Lotus 1-2-3 was constructed to perform the triangular  $(a, b, c)$  coordinate transformation to the required cartesian  $(X, Y)$  coordinate system. Details of the equations of transformation and their derivation are shown in the Appendix. For convenience and simplification, the point A is located at the cartesian origin and the line A-C lies on the X axis. This gives the following coordinates  $(X, Y)$  for the three principle phases (Fig. 7):

$$A(0,0) = \text{water}$$

$$B(2\alpha,0) = \text{lead oxide}$$

$$C(\alpha, \sqrt{3}\alpha) = \text{sulphur trioxide}$$

where  $\alpha$  is a convenient scale factor.

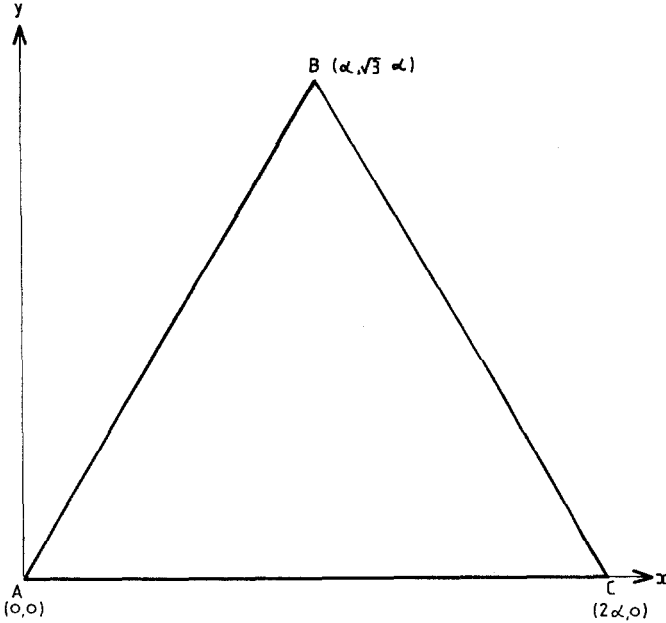


Fig. 7. Relationship between triangular and cartesian coordinates.

TABLE 1

Mathematical rules used to compute paste phase composition

S	Rule
*	$o = ox * (1-\%/100)$
*	$\%PbO = 100 * ox / (ox + w)$
*	$\%H_2O = 100 * w / (ox + w)$
*	$\%PbOf = 100 - (\%H_2Of + \%SO_3f)$
*	$\%H_2Of = (w + k * A) * 100 / (ox + w + g * A)$
*	$\%SO_3f = j * A * 100 / (o + w + g * A)$
*	$\%PbOc = o * 100 / (o + j * A)$
*	$\%SO_3c = j * A * 100 / (o + j * A)$
*	$k = ((100-p) / 100 + .18 * p / 98) * g$
*	$j = .8 * p * g / 98$
*	$p = 125 * (g-1)$
*	$X_4 = (\%PbOc - PbOb_4) / (100 - PbOb_4) * 100$
*	$X_3 = (\%PbOc - PbOb_3) / (100 - PbOb_3) * 100$
*	$F = 80 * \%PbOc / 223 / (100 - \%PbOc) - 1$
*	$M = 100 / H$
*	$H = \sqrt{3}$
*	$\%PbOc = b_3 * 100$
*	$\%SO_3c = c_3 * 100$
*	$\%H_2Oc = a_3 * 100 + .001$
*	$\%PbO = b_1 * 100$

(continued)



TABLE 1 (continued)

S	Rule
*	%H2O = a1*100
*	%SO3 = c1*100 +.001
*	%H2Of = a2*100
*	%PbOf = b2*100
*	%SO3f = c2*100
*	oo = o*(1 + %/100)*223/207
*	%PbOco = oo*100/(oo + j*A)
*	%SO3co = j*A*100/(oo + j*A)
*	%PbOco = b4*100
*	%SO3co = c4*100
*	X3o = (%PbOco-PbOb3)/(100-PbOb3)*100
*	X4o = (%PbOco-PbOb4)/(100-PbOb4)*100
*	Fo = 80*%PbOco/223/(100-%PbOco)-1
*	PbOb0 = 223/(223 + 80)*100
*	SO3b0 = 80/(223 + 80)*100
*	PbOb1 = 2*223/(2*223 + 80)*100
*	SO3b1 = 80/(2*223 + 80)*100
*	PbOb3 = 4*223/(4*223 + 80)*100
*	SO3b3 = 80/(4*223 + 80)*100
*	PbOb4 = 5*223/(5*223 + 80)*100
*	SO3b4 = 89/(5*223 + 80)*100

TABLE 2

Calculated phase composition of paste

St	Input	Name	Output	Unit	Comment
					MODEL NAME NEWPSTE.TK
					After Solve reset RULE sheet & delete
					VARIABLE sheet except the a,b,c,'s. Sav
					Load TRI ALL.TK and combine with
					TEMP 3
	1000	ox		Kg	Oxide weight
	25	%			% Free lead
	100	w		1	Water volume
	100	A		1	Acid volume
	1.4	g			Acid S.G.
		o	750	Kg	PbO initial weight
		oo	1009.9638	Kg	PbO final weight
		%PbO	90.909091		Slurry composition
		%H2O	9.0909091		Slurry composition
	0	%SO3			Slurry composition
		%PbOf	79.481450		Formulated composition
		%H2Of	14.746544		Formulated composition
		%SO3f	5.7720058		Formulated composition
		%PbOc	92.920354		Conditioned composition no Pb oxidation

(continued)

TABLE 2 (continued)

St	Input	Name	Output	Unit	Comment
	0	%H2Oc			Conditioned composition no Pb oxidation
		%SO3c	7.0796460		Conditioned composition no Pb oxidation
		X3	13.982301		%PbO- - - - -3.PbO.PbSO4 no oxidation
		X4	-5.752212		%PbO- - - - -4.PbO.PbSO4 no oxidation
		F	3.7085202		Nominal formula F.(PbO).PbSO4. no oxidation
		X3o	34.937550		%PbO- - - - -3.PbO.PbSO4 with oxidation
		X4o	20.010671		%PbO- - - - -4.PbO.PbSO4 with oxidation
		Fo	5.3405797		Nominal formula F.(PbO).PbSO4. with oxidation
		PbOb0	73.597360		PbO, SO3 Various PbSO4s b = 0, 1, 3, 4
		SO3b0	26.402640		PbO, SO3 Various PbSO4s b = 0, 1, 3, 4
		PbOb1	84.790875		PbO, SO3 Various PbSO4s b = 0, 1, 3, 4
		SO3b1	15.209125		PbO, SO3 Various PbSO4s b = 0, 1, 3, 4
		PbOb3	91.769547		PbO, SO3 Various PbSO4s b = 0, 1, 3, 4
		SO3b3	8.2304527		PbO, SO3 Various PbSO4s b = 0, 1, 3, 4
		PbOb4	93.305439		PbO, SO3 Various PbSO4s b = 0, 1, 3, 4
		SO3b4	7.4476987		PbO, SO3 Various PbSO4s b = 0, 1, 3, 4
		%SO3co	5.3549342		Final SO3 %
		%PbOco	94.645066		Final PbO %
		k	.82857143		Water factor of acid
		j	.57142857		SO3 factor of acid
		p	50		% H2SO4 in dil acid
G	.09090909	a1			H2O coordinate
G	.90909091	b1			PbO coordinate
G	.14746544	a2			H2O coordinate
G	.79481450	b2			PbO coordinate
G	.05772006	c2			SO3 coordinate
G	.92920354	b3			PbO coordinate
G	.07079646	c3			SO3 coordinate
G	.94645066	b4			PbO coordinate
G	.05354934	c4			SO3 coordinate

TABLE 3

Mathematical rules for conversion of triangular to cartesian coordinates

S	Rule
*	$M = 100/H$
*	$H = \sqrt{3}$
*	$I3 = (H*x3-y3)/(100-y3)$
*	$J3 = 200*y3/(H*(200-H*x3 + y3))$
*	$R3 = y3/x3$
*	$K3 = 200/(R3 + H)$
*	$a3 = \sqrt{((K3-x3)^2 + (R3*K3-y3)^2)/(K3^2*(1 + R3^2))}$
*	$b3 = \sqrt{(y3^2 + (x3-M*I3)^2)/((M-M*I3)^2 + 100^2)}$
*	$c3 = \sqrt{((x3-J3)^2 + (y3-H*J3)^2)/((200/H-J3)^2 + (H*J3)^2)}$
*	$a3 + b3 + c3 = 1$

(continued)

TABLE 3 (continued)

S	Rule
*	$I1 = (H*x1-y1)/(100-y1)$
*	$J1 = 200*y1/(H*(200-H*x1 + y1))$
*	$R1 = y1/x1$
*	$K1 = 200/(R1 + H)$
*	$a1 = \text{sqrt}(((K1-x1)^2 + (R1*K1-y1)^2)/(K1^2*(1 + R1^2)))$
*	$b1 = \text{sqrt}((y1^2 + (x1-M*I1)^2)/((M-M*I1)^2 + 100^2))$
*	$c1 = \text{sqrt}(((x1-J1)^2 + (y1-H*J1)^2)/((200/H-J1)^2 + (H*J1)^2))$
*	$a1 + b1 + c1 = 1$
*	$I2 = H*x2-y2)/(100-y2)$
*	$J2 = 200*y2/(H*(200-H*x2 + y2))$
*	$R2 = y2/x2$
*	$K2 = 200/(R2 + H)$
*	$a2 = \text{sqrt}(((K2-x2)^2 + (R2*K2-y2)^2)/(K2^2*(1 + R2^2)))$
*	$b2 = \text{sqrt}((y2^2 + (x2-M*I2)^2)/((M-M*I2)^2 + 100^2))$
*	$c2 = \text{sqrt}(((x2-J2)^2 + (y2-H*J2)^2)/((200/H-J2)^2 + (H*J2)^2))$
*	$a2 + b2 + c2 = 1$
*	$I4 = (H*x4-y4)/(100-y4)$
*	$J4 = 200*y4/(H*(200-H*x4 + y4))$
*	$R4 = y4/x4$
*	$K4 = 200/(R4 + H)$
*	$a4 = \text{sqrt}(((K4-x4)^2 + (R4*K4-y4)^2)/(K4^2*(1 + R4^2)))$
*	$b4 = \text{sqrt}((y4^2 + (x4-M*I4)^2)/((M-M*I4)^2 + 100^2))$
*	$c4 = \text{sqrt}(((x4-J4)^2 + (y4-H*J4)^2)/((200/H-J4)^2 + (H*J4)^2))$
*	$a4 + b4 + c4 = 1$

TABLE 4

Calculated cartesian coordinates

St	Input	Name	Output	Unit	Comment
					Model Name TRI ALL
					Import TEMP 3.TK for a, b, c values from
					DO NOT SAVE AFTER SOLVE
G	52.486388	x1		g	
G	90.909091	y1		g	
G	52.555149	x2		g	
G	79.983282	y2		g	
G	61.631885	x3		g	X Cartesian Coordinate
G	93.250444	y3		g	Y Cartesian Coordinate
G	60.680001	x4		g	
G	94.899155	y4		g	
	.09090909	a1			H2O coordinate
	.90909091	b1			PbO coordinate
	.14494265	a2			H2O coordinate
	.79983282	b2			PbO coordinate
	.05522453	c2			SO3 coordinate
	.93250444	b3			PbO coordinate
	.06749556	c3			SO3 coordinate
	.94899155	b4			PbO coordinate
	.05100845	c4			SO3 coordinate

## Reference

- 1 H. B. Stephenson, C. L. Hixson, H. S. Long, J. S. Bryson, J. D. Purdum and E. J. Richie, Pastes and Grids for the Lead-Acid Battery, *ILZRO Project LE-82/LE-84*, Final Report, Dec. 31, 1971, Int. Lead Zinc Res. Org. Inc.

## Appendix

### *Triangular to cartesian coordinate conversion*

Consider Fig. 1

Intermediate defined variables:

$$I = \frac{\alpha(\sqrt{3x_1 - y_1})}{(\sqrt{3\alpha - y_1})} \quad (\text{A})$$

$$J = \frac{2\sqrt{3\alpha}}{(y_1 - \sqrt{3x_1} + 2\alpha\sqrt{3})} \quad (\text{B})$$

$$K = \frac{2\sqrt{3\alpha}}{(R + \sqrt{3})} \quad (\text{C})$$

$$R = \frac{y_1}{x_1} \quad (\text{D})$$

Equation of a straight line:

$$y = mx + c$$

Eqn. line BT

$$m = \frac{(\sqrt{3\alpha - y_1})}{(\alpha - x_1)}; \quad c = \frac{\alpha(y_1 - \sqrt{3x_1})}{(\alpha - x_1)}$$

Therefore

$$y_{BT} = \frac{(\sqrt{3\alpha - y_1})}{(\alpha - x_1)} x + \frac{\alpha(y_1 - \sqrt{3x_1})}{(\alpha - x_1)} \quad (1)$$

Eqn. line CR

$$m = \frac{y_1}{(x_1 - 2\alpha)}; \quad c = \frac{-2\alpha y_1}{(x_1 - 2\alpha)}$$

Therefore,

$$y_{CR} = \frac{y_1}{(x_1 - 2\alpha)} x + \frac{-2\alpha y_1}{(x_1 - 2\alpha)} \quad (2)$$

Eqn. line AS

$$m = \frac{y_1}{x_1}; \quad c = 0$$

Therefore,

$$y_{AS} = \frac{y1}{x1} x \quad (3)$$

Eqn. line AB

$$m = \sqrt{3}; c = 0$$

Therefore,

$$y_{AB} = \sqrt{3}x \quad (4)$$

Eqn. line AC

$$m = 0; c = 0$$

Therefore,

$$y_{AC} = 0 \quad (5)$$

Eqn. line BC

$$m = -\sqrt{3}; c = 2\sqrt{3}\alpha$$

Therefore,

$$y_{BC} = -\sqrt{3}x + 2\sqrt{3}\alpha \quad (6)$$

*Coordinates*

Point R

Meeting point lines AB and CR

Solving eqns. (2) and (4) simultaneously

$$R_{(x, y)} = (J, \sqrt{3}J) \quad \{\text{eqn. (B)}\}$$

Point S

Meeting point lines AS and BC

Solving eqns. (3) and (6) simultaneously

$$S_{(x, y)} = (K, RK) \quad \{\text{eqns. (C), (D)}\}$$

Point T

Meeting point lines AC and BT

Solving eqns. (1) and (4) simultaneously

$$T_{(x, y)} = (I, 0) \quad \{\text{eqn. (A)}\}$$

*Fractional composition*

$$a = \frac{PS}{AS} \longrightarrow a^2 = \frac{PS^2}{AS^2}$$

$$a^2 = \frac{\{(K - x1)^2 + (RK - y1)^2\}}{(K^2 + R^2K^2)}$$

$$b = \frac{PT}{BT} \longrightarrow b^2 = \frac{PT^2}{BT^2}$$

$$b^2 = \frac{\{(I - x_1)^2 + y_1^2\}}{\{(I - \alpha)^2 + (\sqrt{3}\alpha)^2\}}$$

$$c = \frac{PR}{CR} \longrightarrow c^2 = \frac{PR^2}{CR^2}$$

$$c^2 = \frac{\{(J - x_1)^2 + (\sqrt{3}J - y_1)^2\}}{\{(J - 2\alpha)^2 + (\sqrt{3}J)^2\}}$$