5.2 Visualizing the Process of Finding the Convex Hull of a Set of Points in N-Dimensional Space.

The surface of a convex hull of a set of points in n-dimensional space can be thought of as the intersection of all the support hyperplanes of this set. A support hyperplane is the hyperplane that contains at least one point of the set and is such that all the other points in the set lie either in or on one side of the hyperplane. If the set of points is convexly independent, then the support hyperplane can at most contain n points. Thus to define a hyperplane in n-dimensional space one would need to specify at least n points. The procedure to construct the hull numerically can be thought of as follows:

- Find an extreme point of the set, for example, the point with the largest value of x_1 if the coordinates of the points are $(x_1,x_2,\ldots,x_n)$. This point is then one of the points defining the support hyperplane containing it.

- Tilt the hyperplane [illegible] one finds another point such that the points of the set all [illegible] one side of this plane. Repeat this by tilting the plane in various directions until the hyperplane is specified, that is n points (or more if the set is convexly dependent) lie in this plane. This is equivalent to finding the 'flat' surface upon which the set of points could rest, as we did in three dimensions when placing the wire on the table.

- To find how all the points defining the support hyperplane are connected, one must in turn find the convex hull of these points. The convex hull of the face contained in the support hyperplane, which is a surface of dimension (n-1), will in turn be defined by the intersection of the support hyperplanes of dimension (n-2). These are the support hyperplanes to the convex hull above, that is the one contained in the surface of dimension (n-1). This process is repeated into lower and lower dimensions until one finds the lines (of dimension one) defining the edges of the planes (of dimension two) as was done in the three dimensional convex hull program.

- The next step would be to calculate the next support hyperplane of the set of points. The intersection of two support hyperplanes of dimension (n-1) would be a hyperplane of dimension (n-2). This hyperplane would define the edge between the two support hyperplanes. Thus in order to find the next support hyperplane of the set of points, one would take an edge (of dimension (n-2)) of a known support hyperplane (of dimension (n-1)). This edge would also be contained in the new, adjacent support hyperplane, and thus the (n-1) points (or more if the set is convexly dependent) defining this edge would also be contained in the adjoining support hyperplane. One would then tilt this adjoining support hyperplane to find the other point (or points if the set is convexly dependent) that defines it. Thus one could determine the adjacent support hyperplane. One would then repeat the previous step on this hyperplane, until all the straight lines defining the edges of the two dimensional planes of the surface where found.

This algorithm is described in more detail by Swart (1985).

Thus in principal the convex hull of a set of points in any dimension could be found. We will assume in the subsequent discussion that at most n points lie in a hyperplane, that is that the set of points is convexly independent. This is not a limitation, as if more than n points lay in a hyperplane, one could find the convex hull of the points lying in the hyperplane and modify the algorithim accordingly as described above. Thus for a convexly independent set of points, at most n points will lie in a support hyperplane. The edges of the face contained in this support hyperplane will contain (n-1) points and the edges of these in turn (n-2) points and so on. This idea will enable us to predict what the convex hull of a convexly independent curve will look like.

In this problem, we are concerned with finding the convex hull of curves in higher dimensions. In our case each point has a reaction vector associated with it. Let us repeat the above construction with this in mind. We find an extreme point. The reaction vector of this point would have to lie in the support hyperplane if all the points of the curve are to lie on one side of the plane. We would next tilt the plane to find the another

point that lay in that face. By a similar argument, both the point as well as the reaction vector at the point (assuming the point were not an end point) would both need to lie in the hyperplane.

Thus for n even, (n/2) points and the associated (n/2) reaction vectors could define the support hyperplane. However for n odd, either (n-1)/2 points and (n-1)/2 reaction vectors and an end point could define the support hyperplanes, or else a degeneracy in the structure would be needed in order that (n+1)/2 points and (n+1)/2 reaction vectors defined the surface. (Note that (n-1)/2 is an integer number for n odd, and (n+1)/2 in then the next integer number). This is equivalent to (n+1) points defining a surface of dimension (n-1), and thus a degeneracy is needed in order for the extra point to be coplanar to the other n points. Thus it is possible for there to be a large difference in the properties of attainable regions in even dimensions to that of odd dimensions. This seems rather surprising from a chemical engineering view point, but is not that unexpected a result from a mathematical view as it is found, for example, that the behaviour of solutions of certain types of differential equations depends on whether the dimension of the problem is even or odd. RESULT 46

The edges of the support hyperplane would be surfaces of dimension (n-2). These edges would be common to two support hyperplanes. The edge would contain all but one of the points or reaction vectors of the adjacent support hyperplanes, in other words, (n-1) points and reaction vectors would be common to two intesecting support hyperplanes of the convex hull. One might ask how many edges would a support hyperplane have. In two dimensions each of the support lines had two neighboring support lines; in three dimensions each support plane had three neighbouring support planes. By extension, an (n-1) dimensional support plane would presumably have n edges and thus n neighbouring support hyperplanes.

Let us look at what the above discussion implies when constructing the hull. We will look at even and odd dimensions separately. We will let $\underline{C}_i$ be a point on the curve. Then $\underline{C}_{i+1}$ is the neighbouring point of $\underline{C}_i$ in the direction of increasing space time. $\underline{C}_{i-1}$ is the neighbouring point of $\underline{C}_i$

on the other side, ie decreasing space time. In the limit, if $\underline{C}_i$ and $\underline{C}_{i+1}$ lay in a plane, this would imply that the point $\underline{C}_i$ and the reaction vector at that point lay in the plane. Furthermore $\underline{C}^\circ$ is an end point of the curve, and in particular, $\underline{C}_f^\circ$ is the feed point or the initial point of the curve, and $\underline{C}_e^\circ$ is the end or equilibrium point.

Let us firstly consider a support plane in four dimensional space. Four points are thus needed to define a support hyperplane. We will speculate as to what is the most likely convex hull of a convex plug flow trajectory in the same manner as was done in the three dimensional case. The trajectory of the reactor will be regarded as a set of points $\{\underline{C}_i\}$. We will try to determine what the support hyperplane at some point $\underline{C}_i$ on the plug flow trajectory looks like. As the reaction vector as well as the point on the curve must lie in the plane, if a point lies on the plane, so to must the neighbouring point. Thus, the minimum requirements (minimum in that no extra conditions which require a degeneracy of the curve) are as follows:

Case 1: $\underline{C}_i$, $\underline{C}_{i+1}$, $\underline{C}_j$ and $\underline{C}_{j+1}$ define the support hyperplane. In other words, in the limit, the support hyperplane is a structure between two unconnected points on the curve containing the two points as well as the reaction vectors at the points.

Case 2: $\underline{C}_{i-1}$, $\underline{C}_i$, $\underline{C}_{i+1}$, and $\underline{C}^\circ$ define the support plane. In this case we are assuming that the fan structure that was found in three dimensions will also exist in four dimensions. Notice that if this is the case, at least three neighbouring points on the curve are to lie in the support hyperplane. In the limit, this is equivalent to the reaction vector and the derivative of the reaction vector lying in the support hyperplane.

Case 3: $\underline{C}_i$, $\underline{C}_{i+1}$, $\underline{C}_f^\circ$ and $\underline{C}_e^\circ$ lie in the suppor hyperplane. Thus, in the limit, the two end points of the curve as well as a point on the curve and the associated reaction vectors lie in the support hyperplane.

Now each of these is feasible as it satisfies the condition that the curve lies on one side of the support hyperplane locally (as the point as well as the reaction vector lies in the plane). To further decide on which of the three cases is the most likely structure to occur in f dimensions, one must now consider the edges of these proposed support hyperplanes and determine the neighbouring support hyperplanes. There are four edges of a (three dimensional) support hyperplane. These edges are planes (ie two dimensional surfaces), and three points are needed to define these. Obviously the adjoining support hyperplane to these edges must be such that the reaction vector at a point in the edge must lie in the both support hyperplanes. Using this idea we will regard each of the three cases proposed above and see which of these cases are feasible in light of this.

Points	Edges	Neighbouring Support Hyperplane Contains Edge &	
Case 1:			
$\underset{\sim}{C}_i;\underset{\sim}{C}_{i+1};\ \underset{\sim}{C}_j;\ \underset{\sim}{C}_{j+1}$	$\underset{\sim}{C}_i;\underset{\sim}{C}_{i+1};\underset{\sim}{C}_j$	$\underset{\sim}{C}_{j-1}$	I
	$\underset{\sim}{C}_i;\underset{\sim}{C}_{i+1};\underset{\sim}{C}_{j+1}$	$\underset{\sim}{C}_{j+2}$	II
	$\underset{\sim}{C}_i;\underset{\sim}{C}_j;\underset{\sim}{C}_{j+1}$	$\underset{\sim}{C}_{i-1}$	III
	$\underset{\sim}{C}_{i+1};\underset{\sim}{C}_j;\underset{\sim}{C}_{j+1}$	$\underset{\sim}{C}_{i+2}$	IV
Case 2:			
$\underset{\sim}{C}_{i-1};\underset{\sim}{C}_i;\underset{\sim}{C}_{i+1};\ \underset{\sim}{C}^\circ$	$\underset{\sim}{C}_i;\underset{\sim}{C}_{i+1};\underset{\sim}{C}^\circ$	$\underset{\sim}{C}_{i+2}$	I
	$\underset{\sim}{C}_{i-1};\underset{\sim}{C}_i;\underset{\sim}{C}_{i+1}$	$\underset{\sim}{C}_{i+2}$	IIA
	or	$\underset{\sim}{C}_{i-2}$	IIB
	or	$\underset{\sim}{C}^\circ_*$	IIC
	$\underset{\sim}{C}_{i-1};\underset{\sim}{C}_i;\underset{\sim}{C}^\circ$	$\underset{\sim}{C}_{i-2}$	III
	$\underset{\sim}{C}_{i-1};\underset{\sim}{C}_{i+1};\underset{\sim}{C}^\circ$	Not Feasible	IV

where $\underset{\sim}{C}^\circ_*$ is the other end point.

Points	Edges	Neighbouring Support Hyperplane Contains Edge &	
Case 3:			
$\underset{\sim}{C}_i;\underset{\sim}{C}_{i+1};\ \underset{\sim}{C}^\circ_f;\ \underset{\sim}{C}^\circ_e;$	$\underset{\sim}{C}_i;\underset{\sim}{C}_{i+1};\underset{\sim}{C}^\circ_f$	$\underset{\sim}{C}_{i+2}$	IA
	or	$\underset{\sim}{C}_{i-1}$	IB
	$\underset{\sim}{C}_i;\underset{\sim}{C}_{i+1};\underset{\sim}{C}^\circ_e$	$\underset{\sim}{C}_{i+2}$	IIA
	or	$\underset{\sim}{C}_{i-1}$	IIB
	$\underset{\sim}{C}_i;\underset{\sim}{C}^\circ_f;\underset{\sim}{C}^\circ_e$	$\underset{\sim}{C}_{i-1}$	III
	$\underset{\sim}{C}_{i+1};\underset{\sim}{C}^\circ_f;\underset{\sim}{C}^\circ_e$	$\underset{\sim}{C}_{i+2}$	IV

Notice that for Case 2 that edge IV of the face does not have an adjoining support hyperplane. We thus propose that this type of structure is not a feasible support hyperplane. The type of structure as proposed in Case 3 has at least one adjoining support hyperplane for each of the four edges. However some of these adjoining support hyperplanes (in particular those containing edges IA or B and IIA or B) are structures as described for Case 2 and thus these adjoining faces would not be feasible structures as follows from above. Thus it would seem that the structure of the support hyperplanes as proposed for Case 1 is the only possible type of face. The resulting convex hull would be a structure between two non-neighbouring pairs of points on the curve, such that the reaction vector at the points and the two points defined the hyperplane. RESULT 47

Further information would be needed in order to establish if indeed the type of faces classified in Cases 2 and 3 cannot form the convex hull of a strictly convex curve. The principles involved in constructing a convex hull in four dimensions; and the extension thereof to higher, even dimensions; can be seen. Also notice that every time the dimension of the problem is

increased, so to are the number of constraints on the support hyperplanes ie the face of the hull. Thus it does not become easier for a general reactor to lie in the boundary of the attainable region in higher dimensions.

We now consider the possible structure of a convex hull of a convex curve in odd dimensions, and as an example consider the support plane through some point $\underline{C}_i$ in a five dimensional space. Thus $\underline{C}_{i+1}$ would also need to lie in the plane. Notice that we are free to choose three more points. Thus if we choose another point (and the associated reaction vector), this would mean that the remaining point could only be an end point. Alternatively, we could choose three neighbouring points, and then on another part of the curve two neighbouring points The support hyperplane would be a surface of dimension four, and there would be five edges of dimension three.

The following two types of structures are proposed:

Case 1 $\underline{C}_i$; $\underline{C}_{i+1}$; $\underline{C}_j$; $\underline{C}_{j+1}$ and $\underline{C}'$ define the support hyperplane. In other words, in the limit, the support hyperplane is a structure containing two unconnected points on the curve, the associated reaction vectors and an endpoint.

Case 2 $\underline{C}_{i-1}$; $\underline{C}_i$; $\underline{C}_{i+1}$; $\underline{C}_j$ and $\underline{C}_{j+1}$ define the support hyperplane. Thus the proposed support hyperplane is a structure that in the limit, contains two unconnected points on the curve, the associated reaction vectors and the derivative of the reaction vector at one of the points.

Thus repeating the type of argument that was used previously, we can find the edges for the two cases and the adjacent support hyperplanes.

Points	Edges	Neighbouring Support Hyperplane Contains Edge &	
Case 1:			
$\underset{\sim}{C}_i;\underset{\sim}{C}_{i+1};\underset{\sim}{C}_j;\underset{\sim}{C}_{j+1};\underset{\sim}{C}^\circ$	$\underset{\sim}{C}_i;\underset{\sim}{C}_{i+1};\underset{\sim}{C}_j;\underset{\sim}{C}^\circ$	$\underset{\sim}{C}_{j-1}$	I
	$\underset{\sim}{C}_i;\underset{\sim}{C}_{i+1};\underset{\sim}{C}_{j+1};\underset{\sim}{C}^\circ$	$\underset{\sim}{C}_{j+2}$	II
	$\underset{\sim}{C}_i;\underset{\sim}{C}_j;\underset{\sim}{C}_{j-1};\underset{\sim}{C}^\circ$	$\underset{\sim}{C}_{i-1}$	III
	$\underset{\sim}{C}_i;\underset{\sim}{C}_{i+1};\underset{\sim}{C}_j;\underset{\sim}{C}_{j+1}$	$\underset{\sim}{C}^\circ_*$	IVA
	or	$\underset{\sim}{C}_{i-1}$	IVB
	or	$\underset{\sim}{C}_{i+2}$	IVC
	or	$\underset{\sim}{C}_{j-1}$	IVD
	or	$\underset{\sim}{C}_{j+2}$	IVE
	$\underset{\sim}{C}_{i+1};\underset{\sim}{C}_j;\underset{\sim}{C}_{j+1};\underset{\sim}{C}^\circ$	$\underset{\sim}{C}_{i+2}$	V
Case 2:			
$\underset{\sim}{C}_{i-1};\underset{\sim}{C}_i;\underset{\sim}{C}_{i+1};\underset{\sim}{C}_j;\underset{\sim}{C}_{j+1}$	$\underset{\sim}{C}_{i-1};\underset{\sim}{C}_i;\underset{\sim}{C}_{i+1};\underset{\sim}{C}_j$	$\underset{\sim}{C}_{j-1}$	I
	$\underset{\sim}{C}_{i-1};\underset{\sim}{C}_i;\underset{\sim}{C}_{i+1};\underset{\sim}{C}_{j+1}$	$\underset{\sim}{C}_{j+2}$	II
	$\underset{\sim}{C}_i;\underset{\sim}{C}_{i+1};\underset{\sim}{C}_j;\underset{\sim}{C}_{j+1}$	$\underset{\sim}{C}_{i+2}$	IIIA
	or	$\underset{\sim}{C}_{j+2}$	IIIB
	or	$\underset{\sim}{C}_{j-1}$	IIIC
	$\underset{\sim}{C}_{i-1};\underset{\sim}{C}_i;\underset{\sim}{C}_j;\underset{\sim}{C}_{j+1}$	$\underset{\sim}{C}_{i-2}$	IV
	$\underset{\sim}{C}_{i-1};\underset{\sim}{C}_{i+1};\underset{\sim}{C}_j;\underset{\sim}{C}_{j+1}$	Not Feasible	V

where $\underset{\sim}{C}^\circ_*$ is the other end point.

We again reject the Case 2 type of support hyperplane as edge V of this hyperplane is not contained in an adjoining support hyperplane. Thus if we accept that only support hyperplanes of the type described in Case 1 are feasible in five dimensional

space, then we find that we again have a type of fan structure between an end point and the curve, which is a similar result to that found in three dimensions. Note too that the support hyperplane of edge IV would be of type A. If this type of argument is extended to higher, odd dimensions, we can by extension see that the 'fan' structure is likely to be a found in the hulls of all convex curves. RESULT 48

Again it can be seen that the dimension of the problem is increased, so to are the number of constraints on the support faces forming the bounday of the convex hull.

5.3 Properties of the Attainable Region in Higher Dimensions.

All the results derived in Chapter 2 hold in any dimensional space. Thus among the more important results derived in this chapter are:

- Result 1: Locally no combination of mixing and reaction can take us in a direction that does not lie between the mixing and reaction vectors.

- Result 2: The change produced by any differential process of mixing and reaction is confined to lie in the plane (of dimension one) defined by the mixing and reaction vectors.

- Results 4 to 7 for the various idealized reactors.

- All the results for the necessary condition and multiple steady states. Again the only reactors that may not be covered by the necessary condition are those that exhibit branches that are not related to the branches of the C.S.T.R. or recycle reactor locus.

Some of the properties that were found to apply in three dimensional space will also apply in any number of dimensions. Among these are:

- Results 23 and 24: A convex function is one in which all the points along the curve are extremal points and are thus vertices of the convex hull of the function.

- Result 28: For a C.S.T.R., the mixing vector, which must point into the region, is collinear to the reaction vector. Thus a C.S.T.R. in the boundary of the attainable region will always have plug flow reactors leaving it, or in other words, the C.S.T.R. will form bridging points for plug flow trajectories.

- Result 29: By using a similar argument to that above, it can be shown that a differential reactor in the boundary of the region will also form bridging points for plug flow trajectories.

- Results 30 to 33: These results describe the properties of the mixing point of a differential reactor in the boundary of the attainable region. Firstly, only one mixing point is needed for any general differential reactor with only back mixing. This point must lie in the boundary of the attainable region and must be a neighbouring point, a finite distance away from the reactor curve.

- Result 38: With all the above constraints on the mixing point, there can only be a finite number of differential reactors that lie in the boundary of the region along the whole path of the reactor.

- Result 41: For any reactor in the boundary of the region, both the reaction vector and the tangent vector must lie in the boundary of the region, ie they must both be tangential to the surface of the region, along the entire length of the reactor in the boundary of the region.

This last mentioned result is perhaps the most important of the results derived in that it places severe limitations on any reactor that lies in the boundary of the attainable region. Furthermore, as the reaction vector along the curve is tangential to the boundary, plug flow trajectories with feed points on this curve will lie in the boundary of the attainable region in the neighbourhood of the curve.

However, for this to occur, the surface of the attainable region containing this curve must be tangential to the family of plug flow trajectories with feed points along the curve. This is an extension of the idea that was derived in three dimensional space where it was necessary that $\underline{V}\underline{V}\underline{R}$ was tangential to the surface of the attainable region along the feed points of a family of plug flow trajectories in the boundary of the region. As an extension to any dimension it could be speculated as follows:

There are (n-1) vectors $\underline{V}_i$; i= 1,...,(n-1) (including the reaction vector $\underline{R}$) that define the surface of the attainable region in n-dimensional space. Thus in order for the family of plug flow trajectories to be tangential to the surface, we would require that all $\underline{V}_i\underline{V}\underline{R}$ lay in the surface of the region as well. Thus there would be a further (n-1) constraints on any reactor other than a plug flow reactor that was to lie in the boundary of the region. RESULT 49

Let us consider the implications of this for some differential reactor that lies in the boundary of the attainable region. We regard the even and odd dimensional space separately.

Constraints on a differential reactor that lies in the boundary of the attainable in even dimensions.

Let n be the dimension of the space and let n be even. Let $\underline{C}$ be some point along the differential reactor curve and let $\underline{R}$ be the reaction vector at $\underline{C}$. The equation defining a differential reactor is:

$$\frac{d\underline{C}}{d\tau} = q\,(\underline{C}^*-\underline{C}) + \underline{R} \qquad (4.8)$$

where $\underline{C}^*$ is the mixing point. Let $\{\underline{C}_i\}$ and $\{\underline{R}_i\}$; i=1,...(n-2)/2; be the other points and associated reaction vectors defining a support hyperplane of the attainable region at $\underline{C}$. The constraints on the differential reactor are as follows:

- $\underline{C}$; $\underline{R}$; $\{\underline{C}_i\}$ and $\{\underline{R}_i\}$ i=1,...,(n-2)/2 define the support hyperplane.

- if any of the $\{\underline{C}_i\}$ is achieved by a reactor other than a plug flow reactor the tangent(s) of the curve(s) containing the $\underline{C}_i$ must also lie in the support hyperplane.

- the mixing point $\underline{C}^*$ must be in the boundary of the region and directly connected to $\underline{C}$. Thus $\underline{C}^*$ must be a convex combination of $\{\underline{C}_i\}$. Notice how in even dimensions the mixing point of a differential reactor in the boundary of the region will <u>not</u> in general be an end point.

- in order for the support hyperplane to be tangent to the family of plug flow reactors leaving the curve, the change in the reaction vector in any direction along the support hyperplane must be tangential to the plane itself. Thus:

$$\underline{R}_i \nabla \underline{R} \quad \text{and} \quad (\underline{C}_i - \underline{C}) \nabla \underline{R} \qquad i = 1,\ldots,(n-2)/2$$

and

$\underline{R} \nabla \underline{R}$ must lie in the support hyperplane

Thus there are at least (2n-1) constraints on the (n-1) dimensional support hyperplane. In addition every $\underline{C}_i$ that is achieved by a reactor other than a plug flow reactor adds an additional constraint to the hyperplane. Thus a fairly severe degeneracy in the reaction vector would be needed in order for these constraints to be met over a region in the space. RESULT 50

Constraints on a differential reactor that lies in the boundary of the attainable in odd dimensions.

Let n be the dimension of the space and let n be odd. Let $\underline{C}$ be some point along the differential reactor curve and let $\underline{R}$ be the reaction vector at $\underline{C}$. $\underline{C}^\circ$ is one of the feed or equilibrium points of the region and let this point be contained in a support

hyperplane at $\underline{C}$. Let $\{\underline{C}_i\}$ and $\{\underline{R}_i\}$; i=1,...(n-3)/2; be the other points and associated reaction vectors defining the support hyperplane of the attainable region at $\underline{C}$. The constraints on the differential reactor are as follows:

- $\underline{C}$; $\underline{R}$; $\underline{C}^*$; $\{\underline{C}_i\}$ and $\{\underline{R}_i\}$ i=1,...,(n-3)/2 define the support hyperplane.

- if any of the $\{\underline{C}_i\}$ is achieved by a reactor other than a plug flow reactor the tangent(s) of the curve(s) containing the $\underline{C}_i$ must also lie in the support hyperplane.

- the mixing point $\underline{C}^*$ must be in the boundary of the region and directly connected to $\underline{C}$. Thus $\underline{C}^*$ must be a convex combination of $\{\underline{C}_i\}$ and $\underline{C}^\circ$. Notice how in odd dimensions the mixing point of a differential reactor in the boundary of the region can be an end point.

- in order for the support hyperplane to be tangent to the family of plug flow reactors leaving the curve, the change in the reaction vector in any direction along the support hyperplane must be tangential to the plane itself. Thus:

$$\underline{R}_i \nabla \underline{R} \quad \text{and} \quad (\underline{C}_i - \underline{C})\nabla \underline{R} \qquad i = 1,\ldots,(n-3)/2$$

and

$$\underline{R}\nabla\underline{R} \quad \text{and} \quad (\underline{C}^\circ - \underline{C})\nabla\underline{R} \quad \text{must lie in the support hyperplane}$$

Thus there are at least (2n-1) constraints on the (n-1) dimensional support hyperplane. In addition every $\underline{C}_i$ that is achieved by a reactor other than a plug flow reactor adds an additional constraint to the hyperplane. Thus a fairly severe degeneracy in the reaction vector would again be needed in order for these constraints to be met over a region in the space. RESULT 51

Furthermore, the reaction vector and the change in the reaction vector are confined to lie in the support hyperplane at any point on the differential reactor curve that lies in the boundary of the attainable region. Thus this would seem to imply that the reaction vector at the next point along differential reactor

curve would also lie in this support hyperplane. The reaction vector does not as a consequence have a component that can move it out of the hyperplane, and thus it would seem that the differential reactor would be confined to a subspace of the space, and in particular, it could only move in an (n-2) or lower dimensional hyperplane. RESULT 52

If this is indeed the case, the reaction vectors would point backwards along the surface of the hyperplane, and thus the points along the differential reactor could be reached by a family of C.S.T.R.s starting on the edge of the face of the attainable region that corresponded to this hyperplane. This is RESULT 53 an extension of the result that was found in three dimensions. This conjecture is strengthened if one notes if a family of C.S.T.R.'s each touched the boundary of the attainable region at some point, the constraints on this system would be very similar to those described above for the differential reactor.

In higher dimensions it does not become any easier to fulfill all the requirements for a reactor trajectory or locus to lie in the boundary of the region, and thus it can be speculated that in general only plug flow trajectories and C.S.T.R's would form the boundary of the region. RESULT 54

Furthermore, consider a C.S.T.R. that did lie in the boundary of the attainable region in even dimensions. Consider also that there was only one feed point. Now in order for the C.S.T.R. to lie in the boundary, it follows from Result 41 that the reaction vector must be tangential to the surface of the attainable region, and from Result 28 that this reaction vector must be collinear with the mixing vector. Thus the reaction vector must point back along the surface of the region to the feed point of the C.S.T.R., requiring that the feed point not only lie in the boundary of the region, but also that it and the point on the C.S.T.R. locus lie in (n-1) faces of the region. In even dimensions, this would imply, that unless there is degeneracy in the reaction vector, that at most one point along the locus of the C.S.T.R. could lie in the boundary of the region. Otherwise, one would require a region in which the C.S.T.R. locus and the feed point lay in an (n-2) or less dimensional subspace of the space. RESULT 55

In odd dimensions, in comparison, it would be possible for a C.S.T.R. locus to lie entirely in the boundary of the attainable region. This is because of the fan type of structure that can exsist in odd dimensional space. Thus the reaction vector could point backwards along the face of the attainable region towards the feed point, which also be the point from which the fan structure was originating.

RESULT 56

5.4 Conclusions

Some properties of the attainable region have been determined. General properties of the surface are listed above. Furthermore, some of the properties of any reactor that lies in the boundary of the region were also deduced. These ideas clarifiy some of the properties of optimal reactors, and the importance of the reaction vector and the tangent of the reactor curve in defining an optimal reactor.

It has been shown how to construct the attainable region in two and three dimensional space and in principal the region can be constructed in any higher dimension. Convex hull routines do exist, and as the properties of the attainable region are known, a stepwise construction method may be used to find the surface of the region. It can be noted that in general only plug flow reactors and C.S.T.R's will lie in the boundary of the region. The C.S.T.R's will be feed points to plug flow trajectories that lie in the boundary of the region in the neighbourhood of the C.S.T.R. locus.

In general, it will only be possible for other types of reactors to lie in the boundary of the region when there are severe degeneracies in the reaction vector. These degeneracies are needed in order to allow all of the conditions for a reactor to lie in the boundary of the attainable region to be met over a region in the space. Among these conditions are:

- the tangent vector to the reactor curve must lie in the surface of the region.

- the reaction vectors along the reactor curve must also be tangential to the surface of the region. Thus there will always be plug flow trajecories with feed points along the reactor curve that lie in the boundary of the region in the neighbourhood of the curve.

- the surface in which the curve lies must be such that it is tangential to the the family of plug flow trajectories leaving this reactor curve.

The only conditions under which all these constraints are likely to be met are when some of the components of the reaction vector are linearly dependent, as with the enthalpy or temperature variable; when space time is one of the axes of the region with the consequence that the reaction vector is constant in one direction; and when the reaction vector only depends on the compostion of a few species. It is also likely that under these conditions, a family of C.S.T.R's starting on the boundary of the region and each touching the boundary at a point could rather be used to form the boundary.

Many questions have been raised in this thesis, and some new fields have been indicated as potentially interesting areas of research. Among these are:

- the number of and relationship between the multiple steady states of different types of reactors.

- the relationship between the multiplicity behaviour of a single recycle reactor relative to reactors with more complex recycles.

- the proposition that only plug flow reactors and C.S.T.R.'s lie in the boundary of the attainable region. If this is true, it has some far reaching consequences for general optimzation of reactors as it reduces the possible optimal reactor structures that need to be considered to only serial and parallel combinations of plug flow and C.S.T.R.'s.

- there should be a difference in the solution of optimization problems in even and odd dimensions when the objective function is an open contour or surface. This is because of the fan structure that is found in odd dimensions and not in even dimensions. This difference has not yet been found but should be easy to pick up with linear kinetics. Other useful features of this geometric approach to finding the attainable region are that firstly, the optimal reactor structure for an optimzation objective function that depends only on the variables of the attainable region comes directly out of the construction of the region. Secondly, once the attainable region has been found, any optimization which depends only on the variables of the region is relatively straight forward.

The geometric construction approach can also be used to find the constrained attainable region, ie the region that can be achieved using a specified number and type of reactors. The variables that can be considered in the construction include enthalpy (and thus temperature), space time (and thus volume of reactor) and the concentration of the various species that react in the system.

From a mathematical view, further research into the properties of convex hulls of vector functions in vector fields would be useful. This area has not yet been investigated by mathematicians. Now that a use for this has been found, it could possibly stimulate research in this area.

An extension of these concepts to include separation processes would be extemely useful for solving a wider range of chemical engineering problems. The method of inclusion of separation processes is not straightforward as the new variables that are introduced, such as quantities or flow rates of materials, do not obviously obey the mixing rule.

In conclusion, it is unnecessary said that one should never say anything that is incorrect in a thesis. I obviously hope that all the conjectures that have been made are true, but in this type of work, where many of the concepts and applications thereof are new, it has been very difficult to make sure that all these conjectures are correct. It is most likely that much of what has been written will not be true for some cases with pathological kinetics. Perhaps some of what has been conjectured will prove to be over simplifications. However, whatever I have conjectured that is incorrect or not as general as I have implied, will probably provide many, many papers by later researchers in this field proving me wrong. I look forward to these.

APPENDIX 1

VARIOUS THEOREMS ON THE MULTIPLICITY OF REACTORS

Many of the ideas in this Appendix arose from discussions with Professor D. Glasser and Professor C.M. Crowe. Professor C.M. Crowe also helped with setting these theorems out, particularly Lemma A1.1 and Theorem A1.1.

Lemma A1.1:

The following equation has only one solution, between v_1 and v_2, for $Q > 0$ and $v_2 > v_1 > 0$:

$$\underset{\sim}{R}(\underset{\sim}{C}) + (\underset{\sim}{C}^* - \underset{\sim}{C})\, q(v) = Q \frac{d\underset{\sim}{C}}{dv} \qquad \text{(A1.1)}$$

where - $q(v)$ is a continuous non-negative function between v_1 and v_2 and is defined as $q(v) = (dQ/dv)$.

- v is positive and non-decreasing, and represents the volume of the reactor system.

- $Q = M/\rho^\circ$ from equation 4.8; represents the volumetric flow rate of material through the reactor, and $Q(v_1)>0$.

- $\underline{R}(\underline{C})$ is the reaction vector at $\underline{C}$ and is thus a continuous bounded vector function.

- $\underline{C}$ is a concentration (vector) and is a non-negative bounded function.

- $\underline{C}^*$ is a fixed concentration.

Proof

The proof will be handled in two steps. It will firstly be shown that Q(v) has a unique positive solution, and secondly that $\underline{C}(v)$ exists and is unique.

Step 1:

It will be shown that $q(v)=dQ/dv$ has a unique, positive continuous solution for $v \in (v_1,v_2)$ with $0 \leq v_1 < v_2 < \infty$, provided:

- q(v) is continuous for v>0
- $Q(v_1)>0$

Clearly q(v) satisfies the Lipschitz condition trivially since it does not depend on Q. Thus as q(v) is continuous and it satisfies the Lipschitz condition, it implies that Q(v) exists and is unique. Furthermore, $Q(v) > 0$ for $v > v_1$, since $q(v) > 0$ and $Q(v_1) > 0$. Q(v) is also continuous.

Step 2:

It will be shown that the solution of:

$$\frac{d\underline{C}}{dv} = \frac{\underline{R}(\underline{C}) + (\underline{C}^* - \underline{C})q(v)}{Q(v)} = \underline{f}(\underline{C},v) \qquad \text{(A1.2)}$$

exists and is unique provided that $\underline{R}(\underline{C})$ is a continuously differentiable function of $\underline{C}$ for $0 \leq \underline{C} < \infty$ over any closed interval $[v_1,v_2]$ with $v_2 < \infty$.

$\underline{f}(\underline{C},v)$ is continuous since $\underline{R}(\underline{C})$, $q(v)$ and $Q(v)$ are continuous and $Q(v) > 0$.

Also if C_i is the ith component of $\underline{C}$, and R_j is the jth component of $\underline{R}$, then:

$$\frac{df_j}{dC_i} = \frac{dR_j/dC_i}{Q(v)} \qquad \text{for } i \neq j \qquad \text{(A1.3a)}$$

$$\text{and} \quad \frac{df_i}{dC_i} = \frac{dR_i/dC_i - q(v)}{Q(v)} \qquad \text{(A1.3b)}$$

Thus the derivative exists and is continuous given the assumption of $\underline{R}(\underline{C})$.

$$\left|\frac{df_j}{dC_i}\right| \leq \frac{|dR_j/dC_i|}{Q_1} \quad < K > 0 \qquad \text{(A1.3c)}$$

provided dR_j/dC_i is bounded

But, by the assumption, dR_j/dC_i is continuous over any closed interval and therefore is bounded. Thus $\underline{f}$ satisfies the Lipschitz condition.

Therefore $\underline{C}(v)$ exists and is unique over (v_1,v_2) for $\underline{C}(v_1)=\underline{C}_1$. The solution is also continuous.

Theorem A1.1:

Zwietering's Maxiumum-Mixed Reactor Model (MMR) can only exhibit multiple steady states for systems where the residence time distribution tends to infinity.

Proof:

From Lemma A1.1, if $q(v)$ is continuous over a section of the reactor, then $\underline{C}(v)$ is continuous and unique over that section of reactor and therefore no multiple solutions are introduced.

If $q(v)$ is piecewise continuous with a countable number of discontinuities such that the left and right limits are bounded at each, then the existence and uniquness of lemma A1.1 can be applied to each interval of continuity in turn with:

$$Q(v_i^-) = Q(v_i^+)$$

and $\underline{C}(v_i^-) = \underline{C}(v_i^+)$ for v_i a point of discontinuity (A1.4)

If there are step discontinuitues (finitely many) in $Q(v)$ where $q(v_i)=\delta(v-v_i)\delta Q_i$; then there is no reaction in an infinitesimal volume δv but:

$$Q\underline{C}\big|_v + \delta Q_i \underline{C}^* = (Q+\delta Q)\underline{C}\big|_{v+\Delta v} \qquad \text{(A1.5a)}$$

then the existence and uniquness can apply to the next interval with:

$$Q\big|_{v+\Delta v} = Q\big|_v + \delta Q_i \qquad \text{(A1.5b)}$$

$$\underline{C}|_{v+\Delta v} = \frac{Q_v \underline{C}_v + \delta Q_i \underline{C}^*}{Q_v + \Delta Q_i} \qquad \text{(A1.5c)}$$

At the inlet, a step discontinuity simply alters the value of Q at the reactor inlet. Note that the limits of Q and $\underline{C}(v)$ at the right side of an interval with continuous q(v) are defined by continuity of Q(v) and $\underline{C}(v)$.

The one case that is not clearly treated is where q(v) is not bounded, but Q(v) is bounded. No proof for this case has been found, although it would seem that if the jump condition with a step change in Q(v), as described above, does not exhibit multiple solutions, then it is even more unlikely that this case will exhibit multiple solutions.

We thus are asserting that no multiple solutions appear along the reactor, when v>0. Thus any multiple solutions that the reactor does exhibit, must appear from the inital point, ie as v→0.

Now consider firstly the case where the residence time distribution of the MMR is finite. In this case the MMR for the reactor can be modelled with a finite amount (Q_o) of material entering at v=0, where the Zwietering volume is finite. The material that enters the reactor first (ie spends the longest time in the reactor) has the longest residence time of all the material flowing through the reactor. The residence time of this material is ($v_{reactor}/Q_o$) which is finite, and this material does not introduce any multiple solutions. Along the reactor, as described above, no multiple solutions are introduced, and concentration has a unique value. Thus nowhere is multiplicity introduced.

Consider next the case where the residence time distribution does not have an upper limit but tends to infinity. The multiplicity can in fact only arise from either the initial point or if $\underline{C}$ does not tend to a limit as δv→0.

Assume firstly that $\underline{C}$ does tend to a limit as v→0. If q in finite at v=0, in the limit as δv→0, δQ will become infintesimal.

The residence time of this first fluid is $v_{reactor}/\delta Q \rightarrow \infty$ as δv (and δQ) approach zero. The residence time distribution in this situation will be unbounded.

Considering the mass balance in this situation gives:

$$\underline{C}^* q(v\rightarrow 0)\delta v + \underline{R}(\underline{C})\delta v = \underline{C}\, q(v\rightarrow 0)\delta v \qquad \text{(A1.6a)}$$

$$\text{or} \quad \underline{R}(\underline{C})\,\delta v = (\underline{C}-\underline{C}^*)\, q(v\rightarrow 0)\,\delta v = (\underline{C}-\underline{C}^*)\,\delta Q \qquad \text{(A1.6b)}$$

$$\text{thus} \quad \underline{R}(\underline{C})\,\frac{\delta v}{\delta Q} = \underline{R}(\underline{C})\,\frac{1}{q(v\rightarrow 0)} = (\underline{C}-\underline{C}^*) \qquad \text{(A1.6c)}$$

Notice that this is is the equation describing a C.S.T.R. with inlet concentration $\underline{C}^*$, outlet concentration $\underline{C}$ and residence time $(\delta v/\delta Q)$. If we let δv to approach 0 and δQ remains finite, then $\underline{C}$ at v=0 will be equal to $\underline{C}^*$.

If on the other hand we find that as we let δv approach 0 that δQ also approaches 0 and that $(\delta v/\delta Q)$ is finite and non-zero, then the above equation describes a C.S.T.R. with feed $\underline{C}^*$. This will introduce multiplicity when the C.S.T.R. exhibits multiple steady states. This is thus the only place in the model where multiplicity can be introduced and it can only occur if (dv/dQ) is finite and non-zero which in turn can only occur it the residence time distribution tends to infinity.

It is interesting to note that any MMR that exhibits multiplicity will also exhibit a 'jump' condition at v=0, ie at v=0 the concentration is not equal to $\underline{C}^*$.

The case where $\underline{C}$ does not tend to a limit as $\delta v\rightarrow 0$ is discussed by Glasser et al (1986). This behaviour is exhibited by, for example, a recycle reactor where the concentration varies periodically with remaining life. The periodic behaviour is determined by the algebraic form of the equation describing the reactor. This type of behaviour has not been thouroughly investigated and not much is understood as yet regarding prediciting the periodicity and the resulting multiple steady states that this behaviour gives rise to.

Lemma A1.2:

Any process involving forward mixing and reaction only cannot move outside a region that:

1. is convex
2. has no reaction vectors pointing outwards along the boundary, ie all reaction vectors on the boundary that are non-zero either point inwards or are tangential to the boundary.
3. is attainable for some feed point $\underline{C}^{\circ}$.

By forward mixing, we exclude recycles or backmixing, and we only allow mixing with points that can be achieved by mixing and reaction from points that have already been reached.

Proof:

Consider a point inside a region A that can satisifes the conditions listed above.

Reaction of the material causes the concentration to change, but the change, which is in the direction of the reaction vector, is confined to region A (from condition 2 as no reaction vectors point out of the region).

Consider mixing the material at a point with material at another point which lies inside the region (ie can be reached from the feed point). Again the resultant concentration, which must lie on the vector joining the two points, must lie inside the region A (as it is convex).

Now consider a reactor system that causes us to reach point A^* on the boundary of the region. Reaction of the material causes a change in concentration in the direction of the reaction vector, which points inwards or is tangential to the boundary, and the resulting concentration must lie inside or on the boundary of region A. We can mix with any other concentration/s inside the

region and react the resulting mixture. Again mixing moves us in the direction of the mixing vector which points inside the region. In fact by mixing or reaction of any point/s in the region it is impossible to cross the boundary of the region.

Now consider a system where reaction and mixing occur simultaneously. The vector representing the resulting process is the vector sum of the mixing and reaction vectors and therefore must lie in the accute angle between these two vectors. As explained above, neither the mixing or reaction vector point out of the region, and thus the sum of the two vectors must point into region A. Thus simultaneous reaction and mixing does not allow us to cross the boundary of region A either.

Thus reaction only, mixing only or simultaneous mixing and reaction does not allow us to move outside a region that satisfies the conditions listed above.

Theorom A1.2

All reactors with feed $\underline{C}^\circ$, that can be described by a MMR that does not exhibit periodic behaviour, must lie in a region B that:

1. is convex
2. has no reaction vectors pointing outwards along the boundary, ie all reaction vectors on the boundary that are non-zero either point inwards or are tangential to the boundary.
3. is attainable for some feed point $\underline{C}^\circ$.
4. has no reaction vectors pointing back into the region (ie all C.S.T.R. solutions are included in the region)

Proof

As follows from Theorem A1.1 all points along the MMR:

- when the residence time distribution is bounded and
- excluding $v=0$ when the residence time distribution is unbounded,

can be represented by reaction and forward mixing , ie mixing with the feed and simultaneously reacting the resulting mixture. Thus from Lemma A1.2, this process could not move us out of region B as it satisfies the first three conditions above.

We next look at the point $v=0$ for the case when the residence time distribution is unbounded. At this point the concentrations are equal to that of a C.S.T.R. with feed of $\underline{C}^\circ$. However, by the last condition, all of these points are included in region B. Thus as we started in region B, and as the rest of the reactor cannot move us out the region, the reactor is confined to region B.

Thus it follows that all reactors that are described by a MMR, and which do not exhibit periodic behaviour, cannot move outside the region B if the feed to the reactor lies inside region B.

As any process combining forward mixing and reaction cannot cause us to cross the boundary of the region, a reactor with back mixing to a point that lies outside the region must have had jump conditions along the reactor, that is points where the back mixing allowed us to reach a point outside the boundary of the region. We next show that reactors that can be described by the General Mixing Model (GMM), and this includes a very large class of reactors, are also confined to lie in region B of the previous theorem.

Lemma A1.3

The multiple branches (ie steady states) of a reactor trajectory that is described by the GMM and that does not exhibit periodic variations in concentration with remaining life, must arise from fluid behaving as a C.S.T.R.

Proof

Consider a general element of volume along the reactor which has a finite volumetric flowrate flowing through it. The GMM can be visualized as little batches of fluid of varying ages but with the same remaining life flowing through the reactor (and reacting of course). We will consider the batches of fluid flowing into our element of volume; as well as any feed material entering the volume via a side stream . There are several different ways in which the batches and side stream material can interact or behave, and we will consider each of these in turn.

1. At the volume we are considering some of the batches might flow into the element and react without mixing with any other batches. This portion of the fluid we will call (1).

2. Some of the batches could mix together according to the micromixing characteristics of the reactor. This material, called (2), thus mixes together instantaneously and then reacts.

3. We might also add unreacted feed at a side stream. Some of this feed may mix with batches flowing into the element of volume, forming a new batch of material, called (3).

4. The rest of the side stream may not mix but can be vizualized as forming a new little batch(s) of fluid, called (4).

Multiple solutions cannot arise from the fluid (1) as this fluid behaves as a batch reactor which does not exhibit multiplicity. Fluid (2) is simply the instantaneous mixing of two streams and then the reaction of the resulting mixture. Neither of these processes can cause multiplicity. Fluid (3) cannot exibit multiplicity as this fluid can be described by a mass balance as given in equaton (A1.1) and, as shown in Theorem A1.1, this equation has only one solution for all finite flowrates.

The only multiplcity that can in fact arise is when a little element behaves as a C.S.T.R. By the nature of the model, this could only arise from the side streams when an infinitely small amount of material flows into an infinitely small element of volume in such a way that the fluid has a finite residence time.

Notice the multiplicity that could arise from the fluid denoted (4), although it introduces a new solution for the reactor, the solution is a convex combination of the C.S.T.R. branches and material that is achieved by reacton and mixing. As explained the multiplicity could only arise from an infintesimal volume element with an infintesimal amount of feed. If the result of this is mixed with a finite amount of fluid (as would be found at some point along the reactor) this, by the lever arm rule, could not affect the concentration of the stream.

Thus it is only in the initial section of the GMM, where the amount of fluid in the reactor is infintesimal, that this type of multiplicity can introduce new branches. The multiplicity could only arise from the side streams as an initial (ie at v=0) 'jump' condition. At this point (dQ/dv) may be finite (ie the fluid in

the little volume has a finite residence time) and thus multiplicity could arise. (This is explained in Theorem A1.1).

Theorom A1.3

A reactor with feed $\underset{\sim}{C}_f^\circ$ that can be modelled by the GMM, and that does not exhibit periodic variations in concentration with remaining life, is confined to lie inside a region that-

1. is convex
2. has no reaction vectors pointing outwards
3. has no reaction vectors pointing backwards into the region (ie includes all C.S.T.R. solutions with feed points in the region)
4. is attainable for some feed point $\underset{\sim}{C}_f^\circ$.

Proof:

As shown by lemma A1.2, process that involve only forward mixing and reaction, cannot move out of a region that satisfies the above conditions. The only other processes in the GMM is fluid that behaves as a C.S.T.R. However, as the feed to these C.S.T.R.'s lies inside the region, and the solutions of the C.S.T.R.'s lie inside this region, these processes cannot take us out of a region that satisifes the above necessary conditions. Thus all the multiple solutions that a GMM (that does not exhibit periodic behaviour with remaining life) exhibits, are confined to lie inside the region, and thus the GMM does not extend the region.

APPENDIX 2

PROOF FOR CONJECTURE THAT FOR LINEAR KINETICS, THE POINTS OF THE PLUG FLOW TRAJECTORY ARE ALL EXTREMAL POINTS.

By Professor C.M. Crowe

The nomenclature used in this appendix is not included in the main nomenclature. The new symbols are defined where introduced.

Required to show that there does not exist a real value of τ such that:

$$e^{A\tau} = \sum_{i=1}^{p} \mu_i e^{A\tau_i} \qquad \text{(A2.1)}$$

and such that $\mu_i > 0$; $\sum_{i=1}^{p} \mu_i = 1$; $p \geq 2$

with $0 \leq \tau_1 < \tau_2 < \ldots < \tau_p$

provided that:
(a) A has at least 2 distinct non-zero eigenvalues
or
(b) A has one non-zero eigenvalue with index* ≥ 2.

* The index of an eigenvalue is the size of its largest Jordan block or equivalently the degree of its factor $(\lambda-\lambda_k)$ in the minimal polynomial for A.

Notes

1. If p=1, equation (A2.1) holds as an equality with $\tau=\tau_1$, $\mu_1=1$.

2. For simplicity, we will assume A to be a semi-stability matrix- i.e, all eigenvalues are non-positive and any zero eigenvalue has index = 1. We may have an arbitrary number of zero eigenvalues.

3. If there were only one (possibly multiple) non-zero eigenvalue of index =1 , equation (A2.1) can hold as an equality by suitable choice of τ.

Proof:

Assume (A2.1) holds as an equality. Transform A to its Jordan canonical form by similarity transformation:

$$Q^{-1}AQ = J$$

which also transforms:

$$Q^{-1}e^{A\tau}Q = e^{J\tau}$$

Therefore (A2.1) becomes:

$$e^{J\tau} = \sum_{i=1}^{p} \mu_i e^{J\tau_i} \qquad \text{(A2.2)}$$

The νth superdiagonal of $e^{J\tau}$ is composed uniformly of elements:

$$\frac{\tau^\nu}{\nu!} e^{\lambda_k \tau} \quad ; \quad (\nu = 0,1\ldots,p_k-1); \quad \text{where } p_k \text{ is index of } \lambda_k$$

within a Jordan block for eigenvalue λ_k. Equality (A2.2) requires $\tau>0$.

Thus our task is to show that:

$$t^{\nu} e^{\lambda_k \tau} = \sum_{i=1}^{p} \mu_i t_i^{\nu} e^{\lambda_k \tau_i} \qquad \text{(A2.3)}$$

is impossible for any two λ_j, λ_k with $\lambda_j \neq \lambda_k$;

and for any λ_k with $p_k \geq 2$.

We use Theorem 96 of Hardy et al. (1934):

Theorem 96 Hardy et al

If ψ, x are continuous functions and are strictly monotonic with x increasing then:

$$m_\psi < m_x \qquad \text{if } \Phi = x\psi^{-1} \text{ is strictly convex}$$

unless all τ_i are equal. Here:

$$m_\psi = \psi^{-1}\left[\sum_{i=1}^{p} \mu_i \psi(\tau_i)\right]$$

Case (a): $\lambda_j < \lambda_k < 0$

Choose $\psi(\tau) = -e^{\lambda_j \tau}$; $x(\tau) = -e^{\lambda_k \tau}$

Both ψ and x are monotonic and x is an increasing function of τ.

Therefore $\Phi(u) = -\exp\left[\frac{\lambda_k}{\lambda_j} \ln(-u)\right] \quad u \leq 0$

$$= -(-u)^{\lambda_k/\lambda_j}$$

$$\Phi''(u) = -\left[\frac{\lambda_k}{\lambda_j}\right]\left[\frac{\lambda_k}{\lambda_j} - 1\right](-u)^{\lambda_k/\lambda_j - 2}$$

> 0 and is thus strictly convex.

Therefore $m_\psi < m_x$

Therefore $$-\tau^{(j)} = \frac{1}{\lambda_j} \ln\left[\sum_{i=1}^{p} \mu_i e^{\lambda_j \tau_i}\right]$$

$$< -\tau^{(k)} = \frac{1}{\lambda_k} \ln\left[\sum_{i=1}^{p} \mu_i e^{\lambda_k \tau_i}\right]$$

or $\tau^{(k)} < \tau^{(j)}$

Thus no single value of τ satisfies equation (A2.3) for λ_k and λ_j different.

Case (b): One eigenvalue with index $p_k \geq 2$.

We wish to show that equation (A2.3) cannot hold for λ_k and $\nu = 0,1$; that is:

$$e^{\lambda_k \tau} = \sum_{i=1}^{p} \mu_i e^{\lambda_k \tau_i} \qquad \text{(A2.4)}$$

$$\text{and } \tau\, e^{\lambda_k \tau} = \sum_{i=1}^{p} \mu_i \tau_i e^{\lambda_k \tau_i} \qquad \text{(A2.5)}$$

To show this, we make use of an inequality for twice differentiable convex functions.

Suppose $f(\tau)$ is a twice differentiable function of $\tau \in R$ and is strictly convex.

Then $f''(\tau) > 0$

and $f(\tau) \geq f(v) + (\tau - v)\, f'(v)$

with equality only for $v=\tau$. (See Rockafellar (1970); Theorem 4.4).

Choose $f(\tau) = e^{-\tau}$, which is strictly convex.

Therefore $e^{-\tau} \geq e^{-v} + (\tau - v)(-e^{-v})$

$$= e^{-v}(1-\tau+v)$$

Thus, if $\tau \neq v$

$$ve^{-v} < e^{-\tau} + (\tau-1)e^{-v}$$

Set $v=\tau_i$ $(i=1,2,..,p)$; $0 \leq \tau_1 < \tau_2 \ldots < \tau_p$; and so some $\tau_i \neq \tau$.

Therefore $\sum_{i=1}^{p} \mu_i \tau_i e^{-\tau_i} < e^{-\tau} + (\tau-1) \sum_{i=1}^{p} \mu_i e^{-\tau_i}$

Now if τ is such that equation (A2.4) holds, with $\lambda_k \tau_i \to -\tau_i$ and

$$\lambda_k \tau \to -\tau ;$$

$$\sum_{i=1}^{p} \mu_i \tau_i e^{-\tau_i} < \tau\, e^{-\tau}$$

Thus, no value of τ can satisfy equations (A2.4) and (A2.5) simultaneously.

Remarks

In theory, matrix *A* could have indices >1. Thus, for the kinetics:

$$A \overset{k}{\rightarrow} B \overset{k}{\rightarrow} C \overset{k}{\rightarrow} D$$

$$\text{Matrix } A = \begin{bmatrix} -k & 0 & 0 \\ k & -k & 0 \\ 0 & k & -k \end{bmatrix}$$

$$Q = \begin{bmatrix} 0 & 0 & 1 \\ 0 & k & 0 \\ k^2 & 0 & 0 \end{bmatrix} \qquad J = \begin{bmatrix} -k & 1 & 0 \\ 0 & -k & 1 \\ 0 & 0 & -k \end{bmatrix}$$

$$\exp(J\tau) = \begin{bmatrix} e^{-k\tau} & \tau e^{-k\tau} & \tau^2 e^{-k\tau}/2! \\ 0 & e^{-k\tau} & \tau e^{-k\tau} \\ 0 & 0 & e^{-k\tau} \end{bmatrix}$$

APPENDIX 3

PROOF FOR CONJECTURE THAT FOR LINEAR KINETICS, THE CONVEX HULL OF THE PLUG FLOW TRAJECTORY IS A FAN HULL

By Professor C.M. Crowe

The nomenclature used in this appendix is not included in the main nomenclature. The new symbols are defined where introduced.

To show that for $\underset{\sim}{C} \in R_+^3$ (i.e., $\underset{\sim}{C}$ is 3x1, $> \underset{\sim}{0}$),

If $\underset{\sim}{a}^T \underset{\sim}{C}_1 = \zeta$; $\underset{\sim}{a}^T A \underset{\sim}{C}_1 = 0$

and $\underset{\sim}{a}^T \underset{\sim}{C}_2 = \zeta$ for $\underset{\sim}{C}_2 \neq \underset{\sim}{C}_1$

Then

$$\underset{\sim}{a}^T A \underset{\sim}{C}_2 \neq 0 \qquad \text{(A3.1)}$$

A is assumed to be a rate matrix (semi-stability matrix, ie. with eigenvalues ≤ 0). The properties of the eigenvalues of the rate matrix A are discussed at the end of this appendix.

$$\underset{\sim}{C}_i = \exp(A\tau_i)\, \underset{\sim}{C}_f^o \qquad \tau_1 \geq 0 \quad (i=1,2)$$

$$\tau_2 > \tau_1$$

[Note that the proof treats τ_1 and τ_2 symmetrically so no loss is incurred in assuming $\tau_2 > \tau_1$.]

Provisos: The conclusion (A3.1) is trivially true for all $\underline{C}$ if:

(a) $\underline{a}^T A = \underline{0}$ since then $\underline{a}^T \underline{C}_i = \underline{a}^T \underline{C}_f^o = \underline{a}^T \underline{C}_j = \zeta$

and $\underline{a}^T A \underline{C}_i = 0$ for all $\underline{C}_i$

Thus assume $\underline{a}^T A \neq \underline{0}$ (A3.2)

(b) $A \underline{C}_f^o = \underline{0}$ since then

$\underline{a}^T \underline{C}_i = \underline{a}^T \exp(A r_i) \underline{C}_f^o = \underline{a}^T \underline{C}_f^o = \zeta$

and $\underline{a}^T A \underline{C}_i = \underline{a}^T \exp(A r_i) A \underline{C}_f^o = 0$

Thus assume $A \underline{C}_f^o \neq \underline{0}$ (A3.3)

To handle the proof, we need to consider three cases:

(i) A diagonable.
(ii) A has one eigenvalue with index 2 and one with index 1.
(iii) A has one eigenvalue with index 3.

We simplify notation by assuming that A has been transformed to its Jordan normal form:

$$Q^{-1} A Q = J$$

Assume without loss of generality that $r_1 = 0$ and A is the Jordan normal form. Then we cannot assume that the elements of $\underline{C}_i$ are non-negative since they are obtained from the true concentrations by pre-multiplying by Q^{-1}.

Each of the three cases will be separately considered.

Proof:

Case (i) $A = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{bmatrix}$

Given $\underset{\sim}{a}^T [I - \exp(A\tau_2)] \underset{\sim}{C}_1 = 0$ (A3.4)

and $\underset{\sim}{a}^T A \underset{\sim}{C}_1 = 0$

show $\underset{\sim}{a}^T A \exp(A\tau_2) \underset{\sim}{C}_1 \neq 0$ (A3.5)

The proof will be by contradiction.

We will assume that $\underset{\sim}{a}^T A \exp(A\tau_2) \underset{\sim}{C}_1 = 0$ (A3.6)

and find a contradiction.

Expanding the equations:

$$\sum_{i=1}^{3} \alpha_i [1 - \exp(\lambda_i \tau_2)] = 0$$

$$\sum_{i=1}^{3} \alpha_i (\lambda_i \tau_2) = 0 \qquad \text{(A3.7)}$$

$$\sum_{i=1}^{3} \alpha_i (\lambda_i \tau_2) \exp(\lambda_i \tau_2) = 0$$

Define $y_i = -\lambda_i \tau_2 \geq 0 \quad i = 1 \ldots 3$

Then the system of equations (A3.7) becomes:

$$\begin{bmatrix} 1-e^{-y_1} & 1-e^{-y_2} & 1-e^{-y_3} \\ y_1 & y_2 & y_3 \\ y_1 e^{-y_1} & y_2 e^{-y_2} & y_3 e^{-y_3} \end{bmatrix} \begin{bmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \end{bmatrix} = \underline{0} \quad \text{(A3.8)}$$

We need to show that no values of y_1, y_2, y_3 can yield a singular matrix. If the matrix is singular, then there are ζ_1, ζ_2, ζ_3 not all zero such that:

$$\zeta_1(1-e^{-y_i}) + \zeta_2 y_i + \zeta_3 y_i e^{-y_i} = 0 \qquad \text{(A3.9)}$$

Without loss take $0 < y_1 < y_2 < y_3$

If any $y_i = 0$, or $y_i = y_j (i \neq j)$ $\qquad (i,j = 1,2,3)$.

then equation (A3.8) has a non-trival solution since the matrix has rank 2.

Thus for *A* diagonable, all 3 eigenvalues must be distinct <u>and</u> non-zero

Consider $f(y) = \zeta_1 \dfrac{(1-e^{-y})}{y} + \zeta_2 + \zeta_3 e^{-y}$

Thus to satisfy (A3.9) for $y = y_1$, y_2 and y_3 we must have at least two zeroes for $f'(y)$.

$$f'(y) = -\zeta_1 \left(\frac{1 - e^{-y} - ye^{-y}}{y^2} \right) - \zeta_3 e^{-y}$$

$f'(y) = 0 \Rightarrow \zeta_3 \neq 0$, $\zeta_1 \neq 0$ since otherwise either $f'(y)$ is monotonic, or $\zeta_1 = \zeta_2 = \zeta_3 = 0$

Thus set $\zeta_3 = 1$

Clearly $\zeta_1 < 0$ in order that $f(y)$ <u>not</u> be monotonic.

$$f'(y) = 0 \Rightarrow \frac{-1}{\zeta_1} = \frac{(1 - e^{-y} - ye^{-y})}{y^2 e^{-y}}$$

$$= h(y)$$

If $h(y)$ is monotonic, then for any given ζ_1 there is at most one zero of $f'(y)$ and thus at most two solutions to $f(y)=0$.

$$h'(y) = \frac{(y-2)(e^y-1) + 2y}{y^3} \quad ; \quad h'(0) = \frac{1}{6}$$

$$h'(y \to \infty) \to \infty$$

$$h(0) = \tfrac{1}{2} \ , \ h(y \to \infty) \to \infty$$

Now $h'(y) > 0$ iff the numerator > 0

Numerator: $(y-2)(e^y-1) + 2y = 0$ at $y=0$

Derivative is $e^y (y-1+e^{-y}) > 0$ for $y > 0$.

Therefore $h(y)$ is strictly montonic
Therefore $f'(y) = 0$ at most once
Therefore $f(y) = 0$ has at most two solutions

<u>Case(ii)</u> $A = \begin{bmatrix} \lambda_1 & 1 & 0 \\ 0 & \lambda_1 & 0 \\ 0 & 0 & \lambda_2 \end{bmatrix}$

$$\text{I-exp } (A\tau_2) = \begin{bmatrix} 1-e^{\lambda_1\tau_2} & -\tau_2 e^{\lambda_1\tau_2} & 0 \\ 0 & 1-e^{\lambda_1\tau_2} & 0 \\ 0 & 0 & 1-e^{\lambda_2\tau_2} \end{bmatrix}$$

$$A\, e^{A\tau_2} = \begin{bmatrix} \lambda_1 e^{\lambda_1\tau_2} & (1+\lambda_1\tau_2)e^{\lambda_1\tau_2} & 0 \\ 0 & \lambda_1 e^{\lambda_1\tau_2} & 0 \\ 0 & 0 & \lambda_2 e^{\lambda_2\tau_2} \end{bmatrix}$$

Therefore equations (4) to (6) become

$$\alpha_1 \lambda_1 e^{\lambda_1\tau_2} + \alpha_2 (1+\lambda_1\tau_2) e^{\lambda_1\tau_2} + \alpha_3\lambda_2 e^{\lambda_2\tau_2} = 0$$

$$\alpha_1 (1-e^{\lambda_1\tau_2}) - \alpha_2\tau_2 e^{\lambda_1\tau_2} + \alpha_3(1-e^{\lambda_2\tau_2}) = 0$$

$$\alpha_1\lambda_1 + \alpha_2 + \alpha_3\lambda_2 = 0$$

With $y_i = -\lambda_i\tau_2$, the above equations can be written as:

$$\alpha_1 y_1 e^{-y_1} - \alpha_2\tau_2 (1-y_1) e^{-y_1} + \alpha_3 y_2 e^{-y_2} = 0$$

$$\alpha_1 (1-e^{-y_1}) - \alpha_2\tau_2 e^{-y_1} + \alpha_3 (1-e^{-y_2}) = 0$$

$$\alpha_1 y_1 - \alpha_2\tau_2 + \alpha_3 y_2 = 0$$

Again, a solution is obtained if $y_1=0$, or $y_2=0$ or $y_1 = y_2$.

Defining $f(y) = \zeta_1\left(\frac{1-e^{-y}}{y}\right) + \zeta_2 + \zeta_3 e^{-y}$

We have $f(y_1) = f'(y_1) = 0$

$f(y_2) = 0$

Again $\zeta_1 < 0$, $\zeta_3 = 1$

But, as before, we can have only one minimum or maximum for f(y) for a given ζ_1.

At $f'(y) = 0$

$$f''(y) = 2\,\zeta_1\left(\frac{1-e^{-y}-ye^{-y}-\frac{1}{2}y^2e^{-y}}{y^3}\right) + e^{-y}$$

with $\zeta_1 = \frac{-y^2e^{-y}}{1-e^{-y}-ye^{-y}}$

$$f''(y) = e^{-y}\left(\frac{y-2(1-e^{-y})+ye^{-y}}{y(1-e^{-y}-ye^{-y})}\right)$$

$f''(0) = 1/3$

Numerator = 0 at y=0
Derivative is $(1-e^{-y}-ye^{-y}) \geq 0$ for $y \geq 0$
Denominator > 0
Therefore $f''(y) > 0$
So that $f'(y)=0$ gives a minimum

Thus there cannot be two y_i's such that $f(y_1)=0$, $f'(y_1)=0$ and $f(y_2)=0$

Case (iii): $A = \begin{bmatrix} \lambda & 1 & 0 \\ 0 & \lambda & 1 \\ 0 & 0 & \lambda \end{bmatrix}$ $e^{A\tau} = \begin{bmatrix} e^{\lambda\tau} & \tau e^{\lambda\tau} & \frac{1}{2}\tau^2 e^{\lambda\tau} \\ 0 & e^{\lambda\tau} & \tau e^{\lambda\tau} \\ 0 & 0 & e^{\lambda\tau} \end{bmatrix}$

$$Ae^{A\tau} = \begin{bmatrix} \lambda e^{\lambda\tau} & (1+\lambda\tau)e^{\lambda\tau} & \frac{1}{2}(2+\lambda\tau)\tau e^{\lambda\tau} \\ 0 & \lambda e^{\lambda\tau} & (1+\lambda\tau)e^{\lambda\tau} \\ 0 & 0 & \lambda e^{\lambda\tau} \end{bmatrix}$$

Therefore:

$$\alpha_1 (1-e^{\lambda\tau}) - \alpha_2 \tau e^{\lambda\tau} - \alpha_3' \tfrac{1}{2}\tau^2 e^{\lambda\tau} = 0$$

$$\alpha_1 \lambda + \alpha_2 = 0$$

$$\alpha_1 \lambda e^{\lambda\tau} + \alpha_2 (1+\lambda\tau)e^{\lambda\tau} + \alpha_3' (1+\tfrac{1}{2}\lambda\tau)\tau e^{\lambda\tau} = 0$$

Eliminating $\alpha_2 = -\alpha_1\lambda$; $\alpha_3 = \alpha_3' \tfrac{1}{2}\tau^2$ and setting $y = -\lambda\tau$

$$\alpha_1 (1-e^{-y}-ye^{-y}) - \alpha_3 e^{-y} = 0$$

$$\alpha_1 y^2 - \alpha_3 (2-y) = 0$$

Determinant $= y^2 e^{-y} - (1-e^{-y} - ye^{-y})(2-y)$

$$= y - 2(1-e^{-y}) + ye^{-y}$$

which can be shown to be > 0 for $y>0$.

Thus for all three cases, the matrices multiplying the $\{\alpha_i\}$ are structurally non-singular. This implies $\alpha_1=\alpha_2=\alpha_3=0$. Thus there is no non-zero vector $\underline{a}$ which can satisfy the equations:

$$\underline{a}^T (I-e^{A\tau_2}) \underline{C}_1 = 0 \qquad \text{(A3.10)}$$

$$\underline{a}^T A \underline{C}_1 = 0 \qquad \text{(A3.11)}$$

and $\underset{\sim}{a}^T A e^{Ar_2} \underset{\sim}{C}_1 = 0$ (A3.12)

Therefore $\underset{\sim}{a}^T A e^{Ar_2} \underset{\sim}{C}_1 \neq 0$ when (A3.10) and (A3.11) hold.

Remark: This implies that (A3.10), (A3.11) and (A3.12) can hold simultaneously for A at least (4x4) since non-singularity implies solutions for a set of non-homogeneous linear equations.

We have excluded the cases of:

(a) $\underset{\sim}{a}^T A = \underset{\sim}{0}$

(b) $A\underset{\sim}{C}_f^o = \underset{\sim}{0}$

(c) More than one Jordan block with the same eigenvalue.

...

It has been tacitly assumed in the above proof that eigenvalues of matrix A are real. The original proofs of Jost (1947) and Wei and Prater (1962) assumed that no element of the kinetic matrix K was zero. The general case was treated by Prater et al (1967), who indeed showed that the matrix K is similar to a symmetric matrix and thus that the eigenvalues are all real. They are in fact non-positive since the Gershgorin circles for the columns are centered on the negative real axis and pass through the origin.

One minor question which remains is what is the relationship between the eigenvalues of the matrix A obtained from the kinetic matrix K by eliminating one species? One can state that the non-zero eigenvalues of A are identical to the non-zero eigenvalues of K. If the matrix K has several zero eigenvalues, this statement still holds. The rank of A is the same as that of K. A proof of this is given below.

Given a kinetic matrix K which is singular, the eigenvalues of

the matrix A, obtained by eliminating one variable, are identical to those of K excluding one zero eigenvalue.

Thus suppose:

$$K = \begin{bmatrix} P & \underset{\sim}{q} \\ \underset{\sim}{r}^T & s \end{bmatrix} \qquad (nxn) \text{ singular}$$

and that $\underset{\sim}{a}^T K = \underset{\sim}{0}$

Then the elimination of C_n from $\underset{\sim}{C}$ in:

$$\frac{d\underset{\sim}{C}}{d\tau} = K\underset{\sim}{C}$$

can be achieved by noting that $\underset{\sim}{a}^T\underset{\sim}{C} = \underset{\sim}{a}^T\underset{\sim}{C}_f^o = \zeta$.

Then, assuming $\underset{\sim}{a}^T = [\ \underset{\sim}{a}_{n-1}^T \quad 1\ ]$ and $\underset{\sim}{C}^T = [\ \underset{\sim}{C}_{n-1}^T \quad C_n]$

$$C_n = \zeta - \underset{\sim}{a}_{n-1}^T \underset{\sim}{C}_{n-1}$$

Therefore $$\frac{d\underset{\sim}{C}_{n-1}}{d\tau} = P\,\underset{\sim}{C}_{n-1} + \underset{\sim}{q}\,C_n$$

$$= [P \quad -\underset{\sim}{q}\,\underset{\sim}{a}_{n-1}^T\ ]\,\underset{\sim}{C}_{n-1} + \underset{\sim}{q}\,\zeta$$

Now eigenvector $\underset{\sim}{z}$ of K and eigenvalue λ are given by $K\underset{\sim}{z} = \lambda\underset{\sim}{z}$

since $\underset{\sim}{a}^T K = \underset{\sim}{0}$, $\underset{\sim}{a}^T\underset{\sim}{z} = 0$ for $\lambda \neq 0$.

Therefore $P\,\underset{\sim}{z}_{n-1} + \underset{\sim}{q}z_n = \lambda\underset{\sim}{z}_{n-1}$

or $$P\,\underset{\sim}{z}_{n-1} - \underset{\sim}{q}\,\underset{\sim}{a}_{n-1}^T\underset{\sim}{z}_{n-1} = \lambda\underset{\sim}{z}_{n-1}$$

with $\underline{z} = \begin{bmatrix} \underline{z}_{n-1} \\ z_n \end{bmatrix}$

Therefore $[P - \underline{q}\underline{a}_{n-1}^T] \underline{z}_{n-1} = \lambda \underline{z}_{n-1}$

so λ is also an eigenvalue of $A = [P - \underline{q}\underline{a}_{n-1}^T]$

If A still contains singularities, this process can be repeated until a non-singular square matrix is obtained.

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