

THE ATTAINABLE REGION GENERATED  
BY REACTION AND MIXING.

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the Witwatersrand, Johannesburg, in fulfilment of the  
requirements for the degree of Doctor of Philosophy.

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DECLARATION

I declare that this thesis, unless stated otherwise, is my own, unaided work. Professor C.M. Crowe provided Appendices 2 and 3, and advised on Appendix 1. This thesis is being submitted for the Degree of Doctor of Philosophy in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other university.

Diane Hildebrandt

11 day of October 1989

ABSTRACT

The following problem is examined: for a given system of reactions with given kinetics, find all the possible outlet conditions that can be achieved by using any system of steady-flow chemical reactors. The outlet conditions or variables that are considered include concentrations, residence time and temperature. This set of all possible outlet conditions for a given feed was called the Attainable Region by Horn (1964). The boundary of the attainable region is of particular interest as, provided the objective function has open contours over the space of the attainable region, the optimum of a system of steady flow reactors will lie in the boundary of the region. More importantly, the optimal reactor structure can be determined from the reactors that form the boundary of the attainable region.

The properties of reaction and mixing are interpreted geometrically and from this a set of necessary conditions for the attainable region is derived. In particular the region must be convex with non-zero reaction vectors on the boundary either pointing into or tangent to the region. A limited, but powerful, sufficiency condition is also derived.

The attainable region is constructed for both two and three dimensional examples. It is also shown how the region can be constructed when constraints, such as a specified sequence of reactors, are imposed.

The properties of a reactor that lies in the boundary of the attainable region in  $n$ -dimensional space are discussed, and in principle the attainable region can be constructed in any number of dimensions.

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The most important and novel result found is that the method generates the structure of the reactor network that makes up the boundary of the attainable region and hence for many problems the optimal reactor network. This is in contrast to all previous methods where one guessed a network and then optimized it for various parameter values.

It was also found that the optimal reactor configuration would in almost all cases be a series-parallel arrangement of C.S.T.R.'s, plug flow reactors and bypasses.

Furthermore, the geometry of the boundary of the attainable region gives rise to analytical conditions for optimum reactor structures that are otherwise not readily available.

Other interesting results were:

- the boundary of the attainable region has very different properties depending on whether the dimension of the space is even or odd, suggesting that the optimization of systems of reactors in even and odd dimensional space could yield rather different results.

- the geometric optimization of interstage cooling and coldshot reactors firstly gives insight into the known analytical conditions, but furthermore applies under conditions where the simple analytical optimization breaks down.

- the well known properties of plug flow reactors with first order kinetics can be easily explained by the geometric properties of the attainable region.

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To my mother, Hettie Peterson,  
With many thanks for her example and guidance.

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LIST OF RESULTS, THEOREMS AND CONJECTURES

Note: R=Result; T=Theorem; C=Conjecture

The dimension that the result is valid in is indicated on the left hand side under the result number, eg 2-D implies the the result is only valid in two dimensional space.

The Necessary Condition is listed in Section 2.7.1.

Result		Page
R1 n-D	Locally no combination of reaction and mixing can take us in a direction that does not lie between the mixing and reaction vectors.	31
R2 n-D	Locally the change resulting from a combination of reaction and mixing must lie in the plane defined by the mixing and reaction vectors.	31
R3 n-D	The attainable region must be a compact simply connected region and in particular must be convex.	33
R4 n-D	The reaction vector is tangent to the plug flow trajectory at every point.	33
R5 n-D	Plug flow trajectories starting from different initial times but with the other initial conditions the same, are just the same curves but shifted up or down on the time axis.	34
R6 n-D	The C.S.T.R. has the property that the vector between the feed and exit points is collinear with the reaction vector at the exit point.	34

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Result		Page
R7 n-D	The recycle reactor is a plug flow reactor with a feed at an average between the exit point and the given feed point.	35
R8 n-D	The attainable region which satisfies the necessary condition (see Section 2.7.1) cannot be extended by the processes of mixing, a plug flow reactor, a recycle reactor or a C.S.T.R.	38
R9 n-D	If a recycle reactor forms part of the boundary of the attainable region, we can always achieve the boundary points by a plug flow reactor starting inside the region.	39
R10 n-D	Any differential process involving reaction and mixing cannot extend a region that satisfies the necessary condition.	40
R11 n-D	Any series-parallel arrangement of the idealized reactors, or any simple reactor that involves the process of differential reaction and mixing, cannot extend a region that satisfies the necessary condition.	40
R12 n-D	The main branch of a recycle reactor, with feed point inside a region that satisfies conditions (a) and (b) of the necessary condition, cannot leave the region.	40
R13 n-D	If a recycle reactor cannot exhibit more branches than the C.S.T.R., condition (c) of the necessary condition is not needed.	41
R14 n-D	If the necessary condition covered the steady states of a particular type of reactor, it would also cover all series-parallel combinations of the reactor as well.	41



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Result		Page
R15 n-D	It is only where multiple solutions are exhibited that the necessary condition is deficient.	42
R16 n-D	The Maximum Mixedness Reactor Model can only exhibit multiple steady states for systems where the residence time distribution tends to infinity.	42
R17 n-D	The multiplicity in a Maximum Mixedness Reactor must either arise from the initial point or because concentration varies periodically with remaining life, ie does not tend to a limit.	43
R18 n-D	If the multiplicity in a Maximum Mixedness Reactor arises from the initial point, this point must satisfy the C.S.T.R. equation.	43
R19 n-D	Reactors that can be described by the General Mixing Model will either: (i) exhibit periodic behaviour, or (ii) lie inside a region that satisfies conditions (a), (b) and (d) of the necessary condition.	43
T2.1 n-D	Given a region that satisfies conditions (a) and (b) of the necessary condition; a locus of a recycle reactor with fixed recycle ratio $R$ that starts inside the region, and that is continuous in residence time $\tau$ , cannot leave the region.	46
C2.1 n-D	It is not generally possible for a recycle reactor to have branches that do not either tend to the C.S.T.R. limit or that are not connected to branches that tend to the C.S.T.R. limit.	48

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Result		Page
C2.2 n-D	No main branch of any reactor structure can move outside of a region that satisfies conditions (a), (b) and (d) of the necessary condition, if the feed point to the reactor lies inside the region.	51
R20 2-D	A region in two dimensional space, that includes all the branches of the C.S.T.R. loci that start inside the region, cannot have a branch of a recycle reactor locus that lies outside the region if the feed point to the recycle reactor lies inside the region.	54
R21 2-D	The point on a plug flow trajectory in two dimensional space where the convex independence of the curve breaks down, is such that the derivative of the slope of the reaction vector with respect to the variable on the x-axis must be zero.	88
R22 2-D	The boundary of the attainable region in two dimensional space will consist of: (i) neighbouring points where the reaction vector is either tangential or points inwards. (ii) lines from an end point $\underline{C}^{\circ}$ to another point $\underline{C}$ , such that the reaction vector at $\underline{C}$ and the vector $(\underline{C}-\underline{C}^{\circ})$ are collinear. (iii) lines between end points. (iv) lines between two points $\underline{C}_1$ and $\underline{C}_2$ , such that the reaction vectors at $\underline{C}_1$ and $\underline{C}_2$ and the vector $(\underline{C}_2-\underline{C}_1)$ are collinear.	89
R23 n-D	A convex function is one in which all the points of the function are extremal points.	93
R24 n-D	A function is strictly convex if at most n points of the function, where n is the dimension of the space, lie in a (n-1) dimensional hyperplane.	94

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Result		Page
R25 3-D	The convex hull of a curve in three dimensional space will not be a fan structure if: (i) the curve and an end point lie in the plane locally; (ii) an end point and two non-neighbouring points and the associated reaction vectors lie in a plane; (iii) an end point, a point on the curve and the associated reaction vectors lie in a plane.	100
R26 3-D	A necessary condition in three dimensional space for the hull of a plug flow trajectory not to be a fan hull is for equation (4.1) to hold.	100
R27 3-D	A necessary condition in three dimensional space for the hull of any reactor curve not to be a fan hull is for equation (4.3) to hold.	102
R28 n-D	A C.S.T.R. locus in the boundary of the attainable region will always have plug flow trajectories that leave it and extend the region, ie the C.S.T.R. locus will again form bridging points.	103
R29 n-D	A differential reactor locus in the boundary of the attainable region will form bridging points from which plug flow trajectories will start and extend the region.	104
R30 n-D	A differential reactor with only back mixing requires at most one mixing point at any point along the reactor. This point must lie in the already achieved convex hull of the reactor.	108
R31 n-D	The optimal mixing point for a differential reactor must lie in the boundary of the hull.	108

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Result		Page
R32 n-D	Only points that are neighbouring points of the differential reactor locus (ie directly joined to the locus) need be considered as potential mixing points.	109
R33 n-D	The mixing point of a differential reactor must be a finite distance from the reaction point.	110
R34 3-D	If the mixing point of a differential reactor locus $\underline{C}^*$ is achieved by some other reactor, then the tangent to the curve at the mixing point $\underline{T}(\underline{C}^*)$ must lie in the plane of $\underline{R}(\underline{C})$ and $(\underline{C}-\underline{C}^*)$ along the whole differential reactor locus.	110
R35 3-D	If the mixing point $\underline{C}^*$ of the differential reactor varies smoothly and continuously with position, the mixing point would have to vary so that the tangent to the curve through the mixing point $\underline{T}(\underline{C}^*)$ , the reaction vector on the differential reactor locus $\underline{R}(\underline{C})$ and $(\underline{C}-\underline{C}^*)$ was coplanar for every $\underline{C}$ .	111
R36 3-D	If the mixing point of the differential reactor locus is an end point, there is no constraint on either the reaction vector or the tangent vector to any curve at the mixing point.	111
R37 3-D	A differential reactor that lies in the boundary of the attainable region, will in general form a fan hull between the mixing point and the reactor locus. At the locus, the reaction vector will be tangential to the fan structure and plug flow reactors will leave the fan structure tangentially. Along the surface of the fan structure, the reaction vectors will point into the hull.	112

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Result	Page	
R38 n-D	There will only be a finite number of differential reactors that lie in the boundary of the attainable region.	112
R39 3-D	In order for a differential reactor to lie in the boundary of the region, $\underline{V}$ , $\underline{R}$ , $\underline{RVR}$ and $\underline{VVR}$ must be coplanar along the entire reactor locus.	121
R40 n-D	No reaction vector along a reactor locus that lies in the boundary of the attainable region can point into the region.	122
R41 n-D	The reaction vectors along any reactor locus that lies in the boundary of the attainable region must be tangential to the hull, so that plug flow trajectories lie in the boundary of the hull in the neighbourhood of the curve.	122
R42 3-D	The reaction vector at the mixing point $\underline{R}(\underline{C}^*)$ of a differential reactor locus that lies in the boundary of the attainable region must lie in the plane of $(\underline{C}-\underline{C}^*)$ and $\underline{R}(\underline{C})$ .	124
R43 3-D	The points where a family of C.S.T.R.'s touched the boundary of the attainable region would be such that $\underline{R}$ , $\underline{V}$ , $\underline{VVR}$ and $\underline{RVR}$ all were coplanar, where $\underline{V}$ is the vector along the fan structure.	165
R44 3-D	The boundary of the attainable region that contained the curve where the family of C.S.T.R.'s touched the boundary, would be planar and would contain the feed points of the C.S.T.R.'s as well the vectors $\underline{R}$ , $\underline{V}$ , $\underline{VVR}$ and $\underline{RVR}$ along the curve.	165

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Result		Page
R45 3-D	Any curve where a differential reactor lay in the boundary of the attainable region could be reached by a family of C.S.T.R.'s as well.	166
R46 n-D	The structure of the attainable region is different in even and odd dimensioned spaces.	171
R47 n-D	In even dimensions, the hull of a strictly convex curve will be a structure between $n/2$ non-neighbouring pairs of points on the curve, such that the points and the reaction vectors at the points defined the support hyperplane.	174
R48 n-D	In odd dimensional space, the hull of a strictly convex curve will be a structure between $(n-1)/2$ non-neighbouring points and an end point, such that the reaction vectors and the points defined the support hyperplane.	177
R49 n-D	Along any reactor curve, excluding the plug flow trajectory, that lies in the boundary of the attainable region, it is required that all $\underline{V}_i \underline{V}_R$ ( $i=1, \dots, n-1$ ) lie in the surface of the region as well, where $\underline{V}_i$ is a vector defining the support hyperplane at a point along the trajectory.	179
R50 n-D	In order for the support hyperplane to a differential reactor, that lies in the boundary of the attainable region in even dimensional space, to be tangent to the family of plug flow trajectories leaving the reactor, there are at least $(2n-1)$ constraints on the $(n-1)$ dimensional hyperplane.	180

Result		Page
R51 n-D	In order for the support hyperplane to a differential reactor that lies in the boundary of the attainable region in $n$ dimensional space, where $n$ is odd, to be tangent to the family of plug flow trajectories leaving the reactor, there are $(2n-1)$ constraints on the $(n-1)$ dimensional hyperplane.	181
R52 n-D	A differential reactor that lies in the boundary of the attainable region in $n$ dimensional space will be confined to move in a hyperplane of dimension $(n-2)$ or lower.	182
R53 n-D	The curve that is formed by a differential reactor that lies in the boundary of the attainable region can be reached by a family of C.S.T.R.'s starting on the edge of the hyperplane that the differential reactor is confined to.	182
R54 n-D	In general it can be speculated that only plug flow reactors and C.S.T.R.'s lie in the boundary of the attainable region. The only situation where another type of reactor may lie in the boundary of the reactor is if the reactor exhibits multiple steady states that are not covered by the necessary condition.	182
R55 n-D	In even dimensional space, at most one point along the C.S.T.R. locus can lie in the boundary of the attainable region if there is no degeneracy in the reaction vector.	182
R56 n-D	In odd dimensional space it is possible for a C.S.T.R. to lie in the boundary of the attainable region along the entire locus.	183

LIST OF DEFINITIONS AND ABBREVIATIONS

*Definitions*

**Basis Temperature** - temperature of stream when it consists of pure feed material, usually designated  $T_b^0$

**Base Trajectory** - plug flow trajectory  $\underline{C}(\tau)$  from usually the feed condition i.e.  $\tau = \tau^0$ ;  $\underline{C}(\tau^0) = \underline{C}_f^0$ . Any other plug flow trajectory  $\underline{C}(\theta)$  obeys the relationship that at  $\theta = (\tau + \theta^0)$ ,  $\underline{C}(\theta) = \underline{C}(\tau)$

**Convex Function** - a function in which all the points of the function are extremal points and vertices of the convex hull of the function.

**Convex Hull** - the region that can be achieved by mixing every point or combination of points with every other point or combination of points taken arbitrarily from a given set of points. See the definition in Chapter One.

**Differential Reactor** - a reactor in which differential reaction and mixing occur. Specific examples are Zwietering's Maximum Mixedness Reactor and the General Mixing Model Reactor.

**Fan Hull** - when the boundary of the convex hull of a curve is made up of lines from a fixed point to all the other points along the curve, this type of structure is called a fan hull. This type of hull can be seen in Figure 4.6.

**Strictly Convex Function** - is a convex function with the further restriction that at most  $n$  points along the function in an  $n$ -dimensional space lie in a (hyper) plane.



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*Abbreviations*

C.S.T.R.    completely stirred tank reactor  
MMR        maximum mixedness reactor  
GMM        general mixing model

NOMENCLATURE

Roman Letters

A 25

region in space, usually denotes attainable region

- A the rate matrix for first order kinetics
- A,B,C,D,E denotes chemical species,  $A_i$  etc refers to chemical species i
- $\underline{a}$  vector defined in equation (4.35)
- $a_1$  ratio of  $k_3 c_A^\circ/k_1$ , as defined in equation (3.4)
- $a_2$  ratio of  $k_2/k_1$ , as defined in equation (3.4)
- a rate constant used in various rate expressions
- B a region in space, usually based on  $(\underline{C}_f)$
- $\underline{b}$  binormal vector, see equation (4.1a)
- b rate constant used in equation (3.10)
- c an extremal point of the set (X)
- $\underline{C}$  characteristic vector  $(d_1, d_2, \dots, d_n, r, \theta)$ ;  
 $(\underline{C})$  refers to the set of  $\underline{C}$ ;  $\underline{C}_i$  refers to specific condition i. When referring to a trajectory, the subscript refers to the order of the points along the trajectory.
- $\underline{C}^{ex}$  used to denote characteristic vector at exit of reactor in situations where confusion could arise
- $\underline{C}^*$  concentration  $\underline{C}$  achieved by or used for mixing;  
 $\underline{C}_i^*$  refers to a specific concentration that is achieved by or used for mixing
- $\underline{C}^\circ$  end point;  $(\underline{C}^\circ)$  set of end points; in general  $\underline{C}_f^\circ$  is a feed point and  $\underline{C}_e^\circ$  is an equilibrium point
- $\underline{C}(\tau^\circ)$  the value of  $\underline{C}$  at space time  $\tau^\circ$  in the reactor
- $C_i$  ith element of  $\underline{C}$
- $\hat{C}_p$  heat capacity at constant pressure per unit mass;  
 $\hat{C}_p^\circ$  refers to the value of  $\hat{C}_p$  at the reference conditions, usually the feed conditions
- $\hat{C}_p$  mean mean value of the heat capacity at constant

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$\underline{c}$	concentration vector in $n$ space with elements $c_i$ ; $\underline{c}^\circ$ reference concentration of $\underline{c}$ , usually the feed concentration
$c_i$	concentration of species $i$ ; $c_i^\circ$ is the reference concentration of species $i$ , usually the feed concentration
$d_i$	composition variable of species $i$ , defined by equation (2.2); $d_i^*$ refers to a composition variable $d_i$ that is achieved by or used for mixing; $d_i^\circ$ refers to $d_i$ at the reference condition
$f(x)$	function of $x$ used in equation (3.5); $f'(x)$ is the derivative of $f(x)$ with respect to $x$
$\underline{f}$	vector function defined in equation (A1.2), $f_i$ is the $i$ th component of $\underline{f}$ ,
$\underline{g}$	a resultant vector
$H$	the convex hull of the set $\{C\}$
$H$	the Hamiltonian
$\hat{H}$	specific enthalpy per unit mass; $\hat{H}_i$ specific enthalpy per unit mass of stream $i$ ; $\hat{H}^\circ$ reference enthalpy
$\hat{H}_{fi}^\circ$	specific enthalpy of formation per unit mass at reference conditions of species $i$
$\hat{\Delta H}_m$	specific enthalpy of mixing
$\hat{\Delta H}_{rxn\ i}$	specific enthalpy of reaction $i$
$I$	the identity matrix
$J$	curvature in direction of normal to plane of $\underline{R}$ and $\underline{V}$ ; defined in equation (4.12)
$K$	rate constant used in equation (3.10)
$K$	limit used in equation (A1.3c)
$k_i$	rate constant for reaction $i$
$M$	Mass flow of material; $M_i$ mass flow rate of stream $i$ ; $M^*$ mass flow rate of stream designated $*$ , usually stream used for or achieved by mixing
$m_i$	molecular mass of species $i$
$\underline{N}$	normal vector to surface $S$ , ie $\underline{N} = \nabla S$
$n$	number of concentration variables
$n$	dimension of space
$P$	parameter defined in equation (4.1) used to check local break down of the fan structure.
$P_a$	supporting hyperplane to a convex set $\{X\}$
$p$	number of points in linear convex combination

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Q	volumetric flow rate through differential reactor, equal to $M/\rho^0$ , $Q(v)$ is the volumetric flow rate at volume $v$ of the reactor; $Q_0$ is the volumetric flow rate at a specific point
q	amount of side stream added in differential reactor, see equation (4.5)
R	an attainable set on base U
R	recycle ratio
$\underline{R}$	reaction vector in $n+2$ space, as a function of $\underline{C}$ ; sometimes denoted $\underline{R}(\underline{C})$ . $\underline{R}(\underline{C}_i)$ denotes reaction vector at $\underline{C}_i$ , sometimes denoted $\underline{R}_i$
$\underline{R}'$	the derivative of the reaction vector with respect to $\tau$ or the parameter of the curve, ie $\underline{R}' = d\underline{R}/d\tau$
$R_i$	ith element of $\underline{R}$
$\mathbb{R}^n$	real space, dimension n
r	number of reactions
$\underline{r}(\underline{C}, T)$	reaction vector in $n+2$ space, as a function of $\underline{C}$ and T
$\underline{r}$	rate of formation vector in $n$ space, components $r_i$ , also referred to as the rate vector
r	rate of formation; $r_i$ is the rate of formation of species i
S	an attainable set on base U
S	surface in which $\underline{V}$ , $\underline{R}$ and $\underline{VVR}$ are coplanar, defined in equation (4.14)
s	arc length of curve, defined in equation (4.9)
$\underline{T}$	Tangent vector to a curve, thus for a curve $\underline{C}(\tau)$ , $\underline{T}$ is the change in $\underline{C}$ with respect to $\tau$ ; $\underline{T}(\underline{C}^*)$ is the tangent vector at $\underline{C}^*$
T	temperature; $T^0$ refers to reference temperature, usually the feed temperature; $T^*$ refers to temperature that is achieved by or used for mixing
$T_{ad}$	adiabatic temperature rise, defined by equation (3.17)
$T_{in}$	inlet temperature defined by equation (3.15c)
$T_b$	basis temperature, defined by equation (3.17)
t	residence time, defined by equation (2.5b)
U	base of attainable sets R and S
$\underline{V}$	mixing vector, equal to $(\underline{C}^* - \underline{C})$ ; $\underline{V}_i$ is a vector defining a support hyperplane in higher dimensions; $V_i$ ith component of $\underline{V}$

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$v$	volume of reactor; $v_i$ volume of reactor associated with stream or system $i$ ; $v^*$ volume of reactor system associated or used for mixing.
$w_i$	mass fraction of species $i$ ; $w_{ij}$ mass fraction of species $i$ in stream $j$
$X_i$	element of set $(X)$ , in the space $R^n$
$X$	a linear convex combination of $p$ points $X_i$
$x, y, z, w$	normalized concentration of species, $x_0, y_0, z_0, w_0$ are values of $x, y, z$ and $w$ at the reference conditions
$Z$	the adjoint vector

Greek Letters

$\alpha, \beta$	mixing ratios
$\alpha_i$	ratio's used in equation (4.33c)
$X$	a convex set of points
$\partial A$	the boundary of $A$
$\Delta$	differential element
$\Phi$	curve in boundary of attainable region that corresponds to points where family of C.S.T.R.'s touch the boundary
$\varphi$	positive scalar quantity with units of time; $\varphi_f$ is a specific value of $\varphi$
$\gamma$	scalar quantity defined in equation (4.27a)
$\mu_i$	coefficients used in linear convex combination of points, $0 \leq \mu_i \leq 1$ .
$\rho$	density; $\rho^o$ refers to density at the reference conditions
$\theta$	temperature-like variable, defined by equation (2.4); $\theta^*$ denotes $\theta$ of stream achieved by or used for mixing
$\tau$	space time defined by equation (2.3); $\tau^*$ denotes $\tau$ of stream produced by or used for mixing, $\tau_i$ refers to space time of stream or system $i$ ; $\tau^o$ refers to space time of feed to reactor.
$\nu$	stoichiometric coefficient; $\nu_{ij}$ is stoichiometric coefficient of species $i$ in reaction $j$
$\zeta$	scalar quantity defined in equation (4.35)

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*Superscripts*

- o denotes initial or reference condition of a material  
\* denotes value of variable used for or achieved by mixing  
+,- denotes limit in the direction of increasing or decreasing variable

*Subscripts*

- i refers to species i  
1,2 refers to stream 1 or 2  
in refers to inlet conditions  
out refers to outlet conditions  
system refers to property of system

*Brackets*

- (C) refers to set of C, with elements  $C_i$

*Mathematical Notation*

- $\nabla_{\underline{R}}$  matrix with element ij equal to  $dR_i/dC_j$   
 $\underline{A} \cdot \underline{B}$  vector with element i equal to  $(A_j(\partial B_i/\partial C_j))$ ; can be interpreted as the change in  $\underline{A}$  in the direction of  $\underline{B}$ ;  $(\underline{A} \cdot \underline{B})_i$  is the i th component of vector  $\underline{A} \cdot \underline{B}$   
 $R_k^{ij}$  equal to  $(\partial^2 R_k / \partial C_i \partial C_j)$   
 $\underline{R}'$  equal to  $d\underline{R}/dr$   
 $\underline{A} \cdot \underline{B}$  dot or scalar product of vectors  $\underline{A}$  and  $\underline{B}$   
 $\underline{A} \times \underline{B}$  cross or vector product of vectors  $\underline{A}$  and  $\underline{B}$ ,  $(\underline{A} \times \underline{B})_i$  is the i th component of vector  $(\underline{A} \times \underline{B})$

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### NOTE TO THE READER

In writing this thesis, I was faced with trying to do two rather different things: firstly to introduce the concept of the attainable region, explain its usefulness and consequences and to give an overview of the results; and secondly, to try and be rigorous and to prove the results in the standard mathematical way. It is the classic case of trying to see both the forest as well as the trees that make-up the forest. If I tried to show development of the concept of the attainable region with the resulting new geometric interpretation of reaction and mixing and the many results and ideas that flow from this, I could be accused of not being rigorous and mathematical in my approach. If, on the other hand, I tried to be precise and mathematical, I found that I tended to get dragged down with hundreds of lemmas and theorem and proofs, making it extremely difficult for the reader to understand the magnitude, breadth and consequences of the concept of the attainable region. I felt that this approach generally obscured the usefulness and the far reaching results of the attainable region.

I decided to rather take the first option with the reasoning that the I would like the reader to easily gain a good idea of the magnitude and the results of this work, ie to see the forest. However, while wandering through the forest, I wanted to point out the trees as we passed them. The compromise I made, was to mark a result, that is a lemma or theorem, by a note in the right hand margin, for example Result 1, and, if it did not detract from the discussion, I proved it in the main body of the text where the result was stated. Other results, where the proof was more involved, I stated in the text and marked it in the right hand margin, and the proof is either given in an appendix or at the end of the chapter, depending on the length of the proof.

I realize that this is not the way things are done in mathematical texts, but I hope that the way I have tried to present my work, will at least make it easier for the general reader to read and follow. I also hope that it will be seen that rigour is not lost and that the more specialized reader will find all the results and proofs easily.

CHAPTER 1

INTRODUCTION AND LITERATURE SURVEY

1.1 Introduction

An interesting and fundamental problem of chemical reactor engineering is: given a system of homogeneous reactions and the associated kinetics, what is the best system of steady flow reactors to use. The answer to this problem is comprised essentially of three components. Each of these components must be satisfied in order for the solution to exist.

- (i) the concentrations must be achievable.
- (ii) a system of steady flow reactors must be able to produce the material.
- (iii) the resulting product from this system of steady flow reactors must be optimal for all possible achievable outlet concentrations and reactor systems. Optimal would be defined in terms of some objective function.

There are material and thermodynamic constraints which both place bounds on the achievable compositions. These bounds are however upper bounds on the compositions as not all the compositions are achievable due to the kinetic constraints of the reaction system itself. At present the only method of determining which concentrations are achievable in general is a trial and error approach. In this type of approach, a system of reactors, such as recycle reactors or dispersion reactors in series, are proposed and the parameters such as recycle ratio or dispersion coefficients are varied. The optimal operating conditions for this system of reactors is then determined, but there is no way of determining whether this optimum is indeed global.



The difficulty in solving this problem arises thus due to the inseparability at this stage between achievable concentrations and the reactor system. This occurs because the type and sequence of mixing in a reactor system determines the resulting achievable concentrations.

Horn (1964) defined the attainable region as the region in the stoichiometric subspace which could be reached by any possible reactor system. He showed that if one could determine this region, the problem of optimization was essentially solved. A full definition of the attainable region as used by Horn is given in Section 1.3.3. This definition has been expanded for the purposes of this thesis and is given in Section 2.4.

In this thesis, the problem of finding the attainable region will be addressed. Using a geometric approach, the properties of mixing and reaction will be examined. From these properties, some of the characteristics of the attainable region can be determined. It will also be shown how the attainable region can be constructed for two and three dimensional examples, and how the approach can be generalized to any n-dimensional problem. An interesting feature is that the reactor structure can be determined directly from the construction of the attainable region. Thus by tackling the problem of finding the best steady flow reactors for given kinetics via determining the attainable region for the reaction kinetics, all three components of the optimization problem can simultaneously be satisfied.

## 1.2 Introduction to the Literature Survey

The topic of modelling and optimizing chemical reactors is of great importance to chemical engineers, and consequently there has been much research in these fields. A detailed survey of all the literature pertaining to the modelling and optimization of chemical reactors would be nearly impossible, and thus the development of the ideas and concepts that are relevant to this research will be outlined. In particular, the developments that

are important and which have direct bearing on the subsequent research will be highlighted.

The modelling and optimization of reactors seems to have been tackled in two distinct approaches. Firstly, a general modelling approach has been used to describe mixing and reaction. This approach has led to the development of the concept of residence time distributions, micro-mixing and macro-mixing, degree of segregation and general mixing models. An off shoot of these ideas was the idea of defining all the possible concentrations one could achieve using any reactor structure - the attainable region. This led to the development of the concept of the thermodynamically attainable region and the stoichiometrically attainable region, but these regions were just upper bounds on the kinetically attainable region.

The second approach to optimizing chemical reactors was by considering kinetics and then proposing a reactor structure and optimizing the variables such as flowrate, residence times etc. There was no way of deciding if the reactor structure chosen was optimal; and thus many papers pertaining to a given system of reaction kinetics can be found with modifications to the reactor structure being proposed and shown to be better than the previous result. The literature in this field is immense, but has never produced any general results with regards to a priori rules for optimal reactor structures.

Each of these approaches will be discussed separately. A further area that will be discussed is the mathematical concepts that will be used in this thesis.

### 1.3 Reactor Modelling and Optimization by Considering Mixing and Reaction in General.

A review of residence time distribution and micro-mixing is given by Nauman (1981). Shinnar (1986) reviews the use of residence time distributions in the design of reactors. These reviews are comprehensive and discuss the limitations of the use of residence

time distributions and micro-mixing in predicting reactor performance. Thus only a broad outline of the developments in the modelling of mixing in reactors will be given, and only those concepts that are central to this thesis will be outlined and discussed in detail.

The concepts of residence time distribution, or macro-mixing, seems to have first been clearly laid out and analysed by Danckwerts (1953). Danckwerts realized that the residence time distribution was sufficient information to calculate the conversion of a reactor for first order kinetics, but not for other kinetics where the conversion would depend on the point-to-point variation in concentration which was not described by the residence time distribution. Danckwerts (1958) later addressed this problem by analysing the concept of mixing on a molecular scale, or micro-mixing as we now call it. In this paper he developed the idea of degree of segregation and defined it. The upper limit of this was a completely segregated system while the lower limit depended on the residence time distribution of the system.

Zwietering (1959) looked further into this lower limit and defined a condition of maximum mixedness compatible with the residence time distribution. The two limits were shown to be related to when the mixing occurred - the earlier the mixing occurred the less the degree of segregation and the higher the degree of mixedness, whereas conversely, the later the mixing occurred the higher the degree of segregation and the lower the degree of mixedness. There was at this stage a mistaken belief that the limit of conversion for any arbitrary reactor system lay between that defined by the segregated model and the maximum mixedness model. Zwietering also determined the flow configurations for the reactor systems which were compatible with the segregated model and the maximum mixedness model. The latter, the maximum mixedness reactor, will be referred to later in the thesis, and will sometimes be abbreviated as the MMR.

Chauhan et al (1972) considered a single homogeneous, isothermal, constant density reaction. They showed that for any arbitrary residence time distribution, the optimum micro-mixing depended on the convexity property of the rate vector. If the rate

expression  $r$  plotted versus reactant concentration  $c$  was concave down (ie  $d^2r(c)/dc^2 > 0$ ), the maximum mixedness reactor maximized conversion. Conversely, if the rate of reaction was concave up (ie  $d^2r(c)/dc^2 < 0$ ) the conversion was maximized by not allowing any micro-mixing ie keeping the fluid segregated. They had found an important result, in that the convexity of the rate vector determines the type of mixing, but the importance of this result did not seem to be appreciated. This possibly occurred as the result was isolated and did not fit into any extensive theory. As shall later be shown, this result comes directly out of the properties of the attainable region.

In a slightly different vein, Denbigh (1961) introduced the concepts of instantaneous and overall reaction yields. From this simple rules were developed in order to predict the flow configurations that would enhance or suppress consecutive or side reactions. These rules however were not sufficient to predict optimal flow configurations with complex reaction schemes such as the Van de Vusse kinetics (1964).

### 1.3.1 Mixing Models

A more recent approach that was taken in the modelling of reactors, was to try to develop a general model that could incorporate both the macro- and micro-mixing aspects of a reactor. The earlier approaches tried to model the mixing based on physical reality ie trying to incorporate diffusivities, viscosities, models of turbulence etc. Other models rather postulated some mixing mechanism, that had no physical reality, and tried to ascertain the effect of the mixing (for example Zwietering (1984)). This type of approach did not really succeed in describing the mixing characteristics of any arbitrary reactor, but has proved useful in describing non-ideal situations in certain circumstances.

Glasser and Jackson (1984) and Jackson and Glasser (1986) formulated a generalized mixing model which could describe the macro- and micro-mixing patterns for any arbitrary reactor. This

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was based on the generalization of a simple system of splitting and mixing points with plug flow sections between them. The model could successfully describe all maximum mixedness reactors, the axial mixing reactor, networks of plug flow reactors and C.S.T.R.'s and in fact networks of reactors which are the limit of discrete mixing processes. This model will be called the General Mixing Model, and will be sometimes be abbreviated as GMM. The model has as yet not been of use for optimization of reactors as it has proved difficult to use for obtaining bounds on conversions and selectivities.

A useful result from the General Mixing Model is understanding how maximum mixedness reactors can exhibit multiple steady states. It was not shown in Zwietering's original model how this was possible. Using the General Mixing Model (Glasser et al (1986) ) it can be shown that when a maximum mixedness reactor has an unbounded residence time distribution it may exhibit multiple steady states. The argument is as follows: firstly arrange all the material in the reactor in order with respect to remaining life. One can determine the concentration of the material and thus determine how concentration of the material in the reactor varies with respect to remaining life. The surprising result is that when there is material in the reactor with infinite remaining life (or equivalently when the reactor has a residence time distribution that tends to infinity), the concentration need not tend to a limit as the remaining life tends to infinity. In this case the reactor may exhibit multiple steady states and the concentrations will vary periodically with respect to remaining life. This had not been realized by Zwietering and it was erroneously assumed that the concentration must tend to a limit in the derivations. This behaviour, that is the periodic variation with respect to remaining life, will be shown to cause a problem when trying to determine a sufficient condition for the attainable region.

In general, this approach has not been fruitful in determining optimum levels of micro- and macro-mixing in order to maximize selectivities or conversions in a reaction scheme.

### 1.3.2 Optimal Reactor Structures

In this approach the answer to the following question was attempted: given some reaction scheme, what is the reactor structure that would optimize a given function of concentration. The literature in this field is reviewed by Chitra and Govind (1985a and b), the first paper covering isothermal reactors and the second non-isothermal reactor systems.

The usual approach is to assume some network of reactors, the individual reactors being of the type that can approach either a plug flow reactor or completely stirred tank reactor, abbreviated C.S.T.R., as limiting behaviour. Horn and Parish (1967) for example, used the dispersion model, tanks in series model and the Taylor model. Horn and Tsai (1967) studied the effect of global and local mixing, with the emphasis on global mixing. The effects of various types of global mixing could be estimated. In particular it could be predicted whether reactor performance could be improved by the mixing. However it did not help to predict the actual optimal reactor structure.

Jackson (1968) used a system of plug flow reactors with mixing points called source and sink points, in many ways foreshadowing the later work by Jackson and Glasser on the GMM. An interesting result was obtained in that the plug flow reactor in which all reactants are fed in at the feed point is optimal when the adjoint vector of each component takes on its largest value at the reactor inlet. If this is not so, bypassing of reactants is a better reactor strategy. Ravimohan (1971) extended the model of Jackson by allowing local mixing in the network ie incorporating C.S.T.R.'s, plug flows, splitting and sink points.

Paynter and Haskin (1970) assumed that any reactor type could be modelled as an axial dispersion model. The problem was then formulated as an optimal control problem. Chitra and Govind (1985a) used a series of recycle reactors to find the optimal flow configuration that would optimize the yield for various examples. Achenie and Biegler (1986b) generalized this type of approach using a non-linear programming formulation to optimize the reactor network. The network was extended to include

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non-ideal reactors and could include heat removal or addition for non-isothermal cases.

Parulekar et al (1983) considered the cyclical operation of variable volume batch reactors. They allowed the operations of quick filling, slow filling, reaction and complete or partial discharge. Within the framework of optimal control strategies, they identified candidate optimal control theories. The control strategies could also be interpreted in terms of serial arrangements of steady flow reactors. These control strategies were then applied to various reaction systems.

A common problem that arises from all these models is that there is no proof that the reactors that are used and the structures that are used are optimal. Thus it is not shown that the results cannot be improved by some other reactor structure. There is, as a consequence, no systematic approach to determining the best flow configuration. The basic problem with this type of approach is that the mixing in the reactor system, and thus the types of reactor and the structure of the reactor network, determines the conversion. There is the inability in all these approaches to separate mixing and the optimal conversion. Thus if an optimal conversion is determined for a particular reactor structure, there is no way of showing that the conversion would not be improved by using another reactor structure. This leads to the next development.

### 1.3.3 The Attainable Region

Horn (1964) postulated the existence of the attainable region ie: "The attainable region corresponds to the totality of physically possible reactors". Thus for a specified feed and specified system of reactions with kinetics, one would consider the output of every possible type of reactor and all possible combinations of these reactors. The set of all the possible output materials from these reactors would be the attainable region. Furthermore, the region would be such that if a point in the attainable region was used as a feed point to another system of reactors, the output from this system of reactors would also lie in the

attainable region. Horn postulated that if the boundary of this region could be found, the optimum reactor corresponding to any constraints could be found by simple geometric consideration. No general method of finding this attainable region was developed.

Feinberg (1980 and 1987) discussed the concept of the stoichiometric subspace ie the subspace of concentration space that lay within the bounds of the mass balance. An interesting geometric result that arises from this work is that the stoichiometric subspace is a hyperplane in the full concentration space. By full concentration space, we include the concentration of all reactants and products (including any intermediates that are formed during reactions and that affect the rate of reaction) that occur in the reaction scheme. Thus as the attainable region is constrained to lie in the stoichiometric subspace, the attainable region is as a consequence also confined to lie in a hyperplane in the full concentration space. This result has been used in this thesis.

Shinnar (1983 and 1988) and Shinnar and Feng (1985) discussed the thermodynamically attainable region ie the region that could in principle be achieved within the bounds of the second law of thermodynamics. This was found to be a far less severe constraint than that imposed by the kinetics; in other words the kinetically attainable region would lie within the boundary of the thermodynamically attainable region. Furthermore, the thermodynamically attainable region would usually lie within, or correspond to the boundary of the stoichiometric subspace. Thus these regions are upper bounds on the kinetically attainable region as defined by Horn. They do not help us in finding the physically achievable region in space.

#### 1.4 Reactor Optimization Using Specific Kinetics

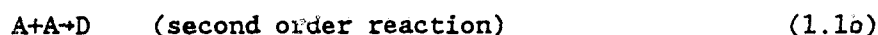
The rules set up by Denbigh (1961), and generalized by Levenspiel (1962), work for the optimization of simple series or parallel kinetics. However these rules do not cover more complex reaction systems and there has been much research into such schemes. The



research is extensive and only the results that are referred to later in this thesis will be highlighted.

#### 1.4.1 Van de Vusse Kinetics

Van de Vusse (1964) suggested a reaction scheme that could not be optimized by simple rules. The kinetics are as follows:



If the objective is to maximize B, then it can be seen that a plug flow reactor would maximize the amount of B formed for the series of reactions described in (1.1a), but a C.S.T.R. would minimize the amount of A used in the side reaction (1.1b). Thus it is not clear what type of reactor would produce the most B.

Gillespie and Carberry (1966) showed that a recycle reactor could produce more B than either a plug flow reactor or C.S.T.R. for certain ranges of the rate constants. De Vera and Varma (1979) classified the entire kinetic parameter space on the basis of maximum yield of B, and thus showed under which conditions the C.S.T.R., plug flow reactor and the recycle reactor are optimal. Lee (1977) extended this analysis and showed that a recycle reactor with the recycle from some intermediate point along the plug flow section could improve the yield of B. Chitra and Govind (1981) optimized this type of recycle reactor over the kinetic parameter space. They found that this reactor structure either gave a plug flow reactor (ie no recycle) or a series combination of a C.S.T.R. and plug flow reactor (ie an infinite recycle from some intermediate point along the reactor) as optimal, depending on the rate constants. Chitra and Govind (1985a) redid the optimization using two standard recycle reactors in series instead. They again found that an intermediate value of the recycle ratio was not optimal and that a serial combination of a C.S.T.R. followed by a plug flow reactor was optimal for the given parameters.

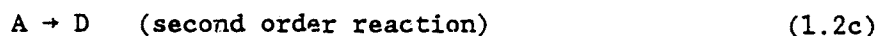
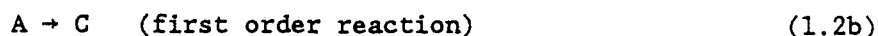
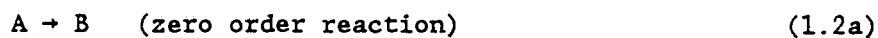
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Achenie and Biegler (1986a) postulated a reactor structure, and the optimization then yielded a plug flow reactor for one of the cases. In the other case, the optimal process was found to be two plug flow reactors in series, with all B removed from the stream leaving the first reactor.

Note that it has not yet been proved what the optimal reactor structure is. Presumably, the type of optimization outlined above could be continued indefinitely, with an infinite variety of reactor structures being postulated and then optimized.

### 1.4.2 Trambouze Kinetics

Another interesting kinetic scheme was suggested by Trambouze and Piret (1959). The reaction scheme is as follows:



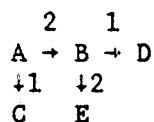
The reactor structure that will optimize the yield or selectivity of C is again not obvious. Trambouze et al considered various reactors, such as a plug flow reactor, a single C.S.T.R., a serial combination of a C.S.T.R. and plug flow reactor, and two C.S.T.R.'s in series. They found that the serial combination of a C.S.T.R. and plug flow reactor gave the highest conversion to C as well as the highest yield (0.495). Paynter and Haskins (1970) assumed that any reactor can be described by an axial dispersion model by allowing the dispersion coefficient to vary appropriately. They then optimized the axial dispersion reactor for the above kinetics, and also found a serial combination of a C.S.T.R. and plug flow reactor to be optimum, with the same selectivity of 0.495 as found by Trambouze et al. Achenie and Biegler (1986a and b) also postulate a dispersion reactor, with varying dispersion coefficient, and found the optimal configuration to be the same as that found by Trambouze et al, but found the optimal selectivity to be 0.4999

### 1.4.3 First Order Kinetics

It was known to Danckwerts (1953), that for linear (that is first order), isothermal kinetics, the conversion of any reactor with known residence time distribution could be calculated as the weighted average of batch reactors, the weighting being proportional to the residence time distribution. Shinnar et al (1973), using an argument based on probability theory, showed that the plug flow reactor is always optimal when the objective function is some convex function of concentration. The proof holds for both non-isothermal and isothermal operation. Glasser et al (1980) examined the properties of the rate matrix, and from these properties were able to show rigorously, among other things, that the plug flow reactor was always better than any cascade of C.S.T.R.'s. By better, we refer to an optimization function that is a linear combination of concentrations leaving the reactor system. The implications of the paper to the design of cascades of C.S.T.R.'s were explained by Glasser and Horn (1980).

### 1.4.4 Denbigh Kinetics

The Denbigh reaction is as follows:



Denbigh (1958) actually assumed all the reactions to be linear, and considered the optimization of the non-isothermal system of reactions. The problem was simplified by considering two C.S.T.R.'s in series rather than a plug flow reactor or any other general reactor structure. The optimal residence time and temperature of each C.S.T.R. was then determined for specified constants.

Chitra and Govind (1985a) modified the reaction slightly, in that they assumed the reaction was isothermal, and that the reactions

were of different orders. The number next to the arrow indicates the orders of reaction that they assumed. Chitra and Govind specified a maximum conversion of 95% to D, and proposed a reactor structure of two recycle reactors in series. This structure was optimized by varying the recycle ratio and the residence times of each reactor. They found a serial combination of plug flow reactor and C.S.T.R. to be optimal.

#### 1.4.5 Westerterp Kinetics

The Westerterp kinetics are:



Kramers and Westerterp (1963) considered various cases for an equimolar feed of A and B, and specified a final degree of conversion of A of 0.95. They found that the plug flow reactor had the smallest volume and the lowest yield of C of all the reactors considered. The C.S.T.R. was next followed by a series of C.S.T.R.'s with distributed feed and a series of plug flow reactors with distributed feed. The best reactor structure was the cross-flow reactor with a feed of B and the A fed in as the side streams. This reactor had the best yield of C but the largest volume of reactor as well.

It is interesting to note at this stage that for all cases when a reactor structure was proposed, such as recycle or axial dispersion reactors in series, the optimization yielded either C.S.T.R.'s or plug flow reactors or a serial combination of these. Thus it would usually appear that only the idealized reactors, such as plug flow reactors or C.S.T.R.'s, are found to be optimum. In the examples where this is found, one would then expect C.S.T.R.'s and plug flow reactors to form either the boundary or at least part of the boundary of the attainable region.

### 1.5 Reactor Structure Optimization

The reactor structures that have probably been most studied and optimized are those of cold shot cooled and interstage cooled reactors. These reactors are practically significant, as many industrially important reactions are highly exothermic, and both cold shot cooled and interstage cooled reactors are practical, easily constructed reactors. Thus the optimization of these two reactor structures will be considered in more detail. As before, a detailed survey of all the literature in this field will not be given, and only the papers that have a direct bearing on this thesis will be discussed.

The interstage cooling reactor consists of a number of adiabatic plug flow reactors in series, with heat exchangers to control the temperature of the feed to each subsequent reactor. The optimization thus must determine the optimal sizes of each reactor and the feed temperature to each reactor for a given feed and reaction. Usually the number of stages and the degree of conversion is also specified.

(1957) and Horn (1961) developed algebraic expressions for interstage cooled reactor. Caha et al (1973) developed a numerical technique to solve the equations to determine the optimal configuration of a three stage reactor with interstage cooling.

The cold shot cooling reactor again consists of a number of plug flow reactors in series. In this reactor however, only the feed to the first reactor is heated, and the temperature control of the feeds to the other plug flow reactors are controlled by bypassing cold feed. This type of reactor is perhaps industrially more important than the interstage cooled reactor, as it is much cheaper to construct as only one heat exchanger is required.

Konoki (1960) derived the equations to minimize the reactor volume of a cold shot cooling reactor. It was assumed that the specific heat or enthalpies of reaction are not functions of temperature. Malenge and Vincent (1972) developed the

generalized equations to maximize the profit of the reactor. The profit was considered to be a function of heat supplied to the reactor system and the amount of catalyst in the system (or equivalently, the volume of the reactor system). The authors also showed how to use the criteria to numerically find the optimal configuration of a three stage cold shot cooling reactor. Again the equations were developed for a system where the enthalpy of reaction was not a function of temperature. Burghardt and Patzek (1978) developed the equations to optimize a cold shot cooling reactor when the upper permissible temperature is specified.

## 1.6 Mathematical Results

Convex hulls and convex functions are a very active field of research at present. Apart from the use of convex hulls in optimization problems, they have found uses in other fields such as robot vision, linear programming and pattern recognition. This field will be shown to be central to determining the attainable region. The concept of a convex hull, and the properties and construction of the convex hull will be discussed in more detail. However, much of the theory that was necessary for the application of convex hulls to attainable regions had not been developed and thus was developed for this thesis.

### 1.6.1 Definition of a Convex Hull and other Mathematical Concepts

There are various equivalent definitions of a convex figure. Some of these will be stated below. These definitions come from Yaglom and Boltyanskii (1961).

*Definition* A figure is called Convex if it wholly contains the line segment that joins any two points of the figure.

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*Definition* A bounded figure is called convex if every line passing through an arbitrary interior point of this figure cuts the boundary in two points.

Also useful is the concept of a support hyperplane.

*Definition* A hyperplane that contains at least one boundary point of a figure and is such that the entire figure lies on one side of the plane, is called a Support Hyperplane of that figure. The support hyperplane thus contains only boundary points and no interior points of the figure.

This concepts leads to a further definition of convex figures.

*Definition* A bounded figure is called convex if through each of its boundary points there passes at least one support hyperplane.

It turns out to be more useful to think of the attainable region as a set of points rather than as a figure. Definitions that are commonly used when working with sets of points are given below. These definitions are taken from Linear Programming by M. Simonnard, translated by W.S. Jewel (1966).

Suppose we have a set of points  $(X)$ , with elements  $X_i$ , in the space  $R^n$ .

*Definition* A Linear Convex Combination of  $p$  points  $X_i$ , called  $C$ , is defined by:

$$C = \sum_{i=1}^p \mu_i X_i \quad \mu_i \geq 0, \quad \sum_{i=1}^p \mu_i = 1$$

*Definition* A Convex Set  $\chi$  of points is such that for any two points  $X_1$  and  $X_2 \in \chi$ ,

$$\mu X_1 + (1-\mu) X_2 \in \chi \quad \text{where} \quad 0 \leq \mu \leq 1$$

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An equivalent definition of a Convex Set is:

*Definition* A set  $X$  is convex if, and only if, for some  $p$ :

$$\left. \begin{array}{l} X_i \in X \quad i = 1, \dots, p \\ \mu_i \geq 0 \quad i = 1, \dots, p \end{array} \right\} \Rightarrow \sum_{i=1}^p \mu_i X_i \in X$$

where  $\sum_{i=1}^p \mu_i = 1$

*Definition* A Convex Hull  $H$  of the set  $(X)$  is the intersection of all the convex sets containing  $(X)$  or

$$\left. \begin{array}{l} X_i \in (X) \\ \mu_i \geq 0 \end{array} \right\} \Rightarrow \sum_{\text{all } i} \mu_i X_i \in H$$

where  $\sum_{\text{all } i} \mu_i = 1$

*Definition* A set of points  $(X)$  is Convexly Independent if

$$\left. \begin{array}{l} X_j, X_i \in (X) \text{ for all } i, i \neq j \\ \mu_i > 0 \quad \text{for all } i, i \neq j \end{array} \right\} \Rightarrow X_j \neq \sum_{\substack{\text{all } i \\ i \neq j}} \mu_i X_i$$

where  $\sum_{\substack{\text{all } i \\ i \neq j}} \mu_i = 1$

In other words, a set is convexly independent if the elements of the set cannot be written as a linear convex combination of the other elements in the set.



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*Definition* An Extremal Point  $c$  of a set  $\{X\}$  is any point which cannot be represented as a linear convex combination with non-zero coefficients of two distinct points of  $\{X\}$ ; i.e. it is impossible to find two points  $X_1$  and  $X_2$  of  $\{X\}$  satisfying:

$$c = \mu X_1 + (1-\mu) X_2, \quad 0 < \mu < 1$$

Notice that only the points of  $\{X\}$  that lie on the boundary or the convex hull of  $\{X\}$  could be extremal points. Consequently, if the set  $\{X\}$  is convexly independent, then all the elements of  $\{X\}$  are extremal points and will be the vertices of the convex hull of  $\{X\}$  (as no more than  $n$  points lie on a hyperplane).

Also notice that from our definition of a Support Hyperplane, we can say: A Support Hyperplane  $P_a$  to a convex set  $\{X\}$  is a hyperplane which contains at least one point of  $\{X\}$  and is such that the points of  $\{X\}$  are on one side of  $P_a$ .

*Definition* The convex hull of the set  $\{X\}$  is thus the intersection of all the support hyperplanes to the convex set.

The ideas above must be extended to the situation where the set  $\{X\}$  is the solution to a continuous function eg the plug flow trajectory. The number of elements of  $\{X\}$  is now uncountably infinite, but this does not affect the basic ideas and properties contained in the above definitions.

Numerical techniques for constructing a convex hull.

This too is a very active field of research at present. Most of the research has been into developing very fast, efficient convex hull routines for planar sets of points. These techniques were not used in this thesis, as it was found quicker to do the examples on a spread sheet, with an interactive approach. Basically, the set of points (such as the plug flow trajectory) was generated on the spreadsheet. This was then plotted and the convex hull determined by looking at the graph. No general, all purpose program was written to construct either a convex hull or attainable region in two dimensions.

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In three or higher dimensions this simple approach is clearly not possible. A program based on that given by Johansen and Gram (1983) was written to determine the convex hull of a set of points in three dimensions. All of the numerical calculation was done on an IBM compatible PC, with a 8087 co-processor. The plots were directly generated and plotted on a Roland DG DXY 880 plotter, that was connected to the computer via the parallel port.

In higher dimensions, there are not that many algorithms to find the convex hull of a set of points, and that outlined by Swart (1985), which is similar in concept to the one used in three dimensions, could be used.

### 1.6.2 Mathematical Structure

Basically it would seem that the problem of finding the attainable region could be rephrased as the following mathematically problem: Given some  $n$ -dimensional space, such that at every point in the space there is an associated vector  $\underline{R}$ , and given some initial point in the space, determine all the points in the space that can be reached using two simple rules. These two rules are related to reaction (ie at any point one can move in the direction of the vector  $\underline{R}$ ) and mixing (that is if we can reach two points in the space, we can also achieve all the points on the line between the two points). These rules or processes will be fully stated and discussed in the next chapter, and so will not be considered in any more detail now.

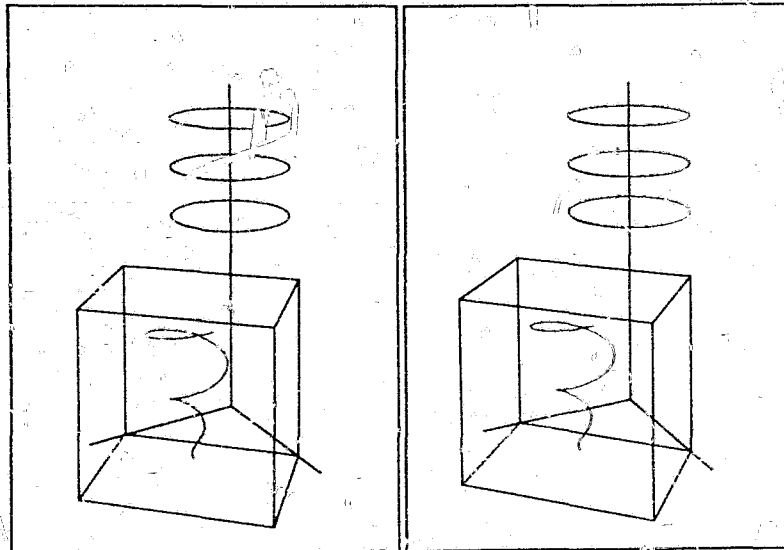
This mathematical problem has not as yet been treated, although there are a class of related problems that are an active area of research at present. One of the related problems is that of stochastic pursuit evasion games, in which two players are given, for example, specified speeds and turning rates, and a strategy of pursuit and evasion must be developed. There is no general solution to this problem, and at present the solution is tackled numerically.

Similarly, it was found that the attainable region could not be found by some a priori approach, that is we could not take some point in the space, and then decide whether or not it could be achieved using the rules of the system. Instead a stepwise construction approach had to be used to determine the attainable region.

### 1.6.3 Stereo Viewing

In order to show the geometric properties of the attainable region in three dimensional space, the construction steps and the final hull are shown in stereo. A stereo viewer is provided in the back pocket of the thesis. A simple projection, based on a pinhole camera, was used to plot the stereo views. The image is projected onto a plane in front of the 'camera' or viewing point. The viewing point is shifted to give a different view of the object. The two images are then viewed one after the other, to give a three dimensional image. An example is given in Figure 1.1. A cube with a spiral inside the cube and three circles stacked above the cube is shown. One should see that the stack of circles as both above and behind the cube; in fact the circles are centered on the green axis. This is however rather difficult to interpret from the stereo views. Instructions for using the viewer are given on the viewer. It may take a bit of practise before the brain is fooled into accepting the images and interpreting them as three dimensional objects.

Figure 1.1 A practice example for stereo viewing



### 1.7 Outline of the Approach used to Determine the Attainable Region

In the next chapter, the rules that described the processes occurring in a chemical reactor, that is mixing and reaction, are outlined and discussed. From these many of the properties of the attainable region can be deduced. Among these are the necessary condition for the attainable region.

In Chapter Three, these conditions will be applied to two dimensional examples. The attainable region will also be constructed for a variety of examples that can be handled in two dimensions, such as the Van de Vusse kinetics, cold shot cooling reactors and interstage cooled reactors.

The approach will be extended to three dimensional examples in Chapter Four, and in particular, the property of convexity, which is obvious in two dimensional space, will be extended to three

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dimensions. Examples will also be done where the attainable region is constructed. The property that the plug flow reactor is always best for linear kinetics when the objective function is a convex combination of concentration, will be proved using geometrical arguments that follow from the properties of the attainable region.

In the final chapter, some of the properties of the attainable region in any  $n$ -dimensional space, and the reactors that would form the boundary of the region, are deduced.

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CHAPTER 2

THE ATTAINABLE REGION : DEFINITION, NECESSARY AND SUFFICIENT  
CONDITION

2.1 Introduction

The attainable region was first defined by Horn (1964) as the region (of outputs) that corresponds to the totality of physically possible reactors. The variables to be incorporated in the region were not defined - but could typically have included concentrations and residence time. The variables that will be included in the definition of the attainable region will firstly be discussed, and thereafter the attainable region will be more precisely defined. By considering the processes of reaction and mixing, it will be shown how the ideal reactors may be geometrically interpreted. From this, the necessary conditions for the region will be derived. As yet, there is not a sufficient condition, but it is known what results are needed in order to derive a sufficiency condition. This will also be discussed.

Many of these results have already appeared (Glasser, Hildebrandt and Crowe (1987) and Hildebrandt, Glasser and Crowe (accepted for publication) ).

It will be assumed that the kinetics do not allow sustained oscillations and that the system is at constant pressure. Non-isothermal, variable density systems are included and the only processes that are allowed are reaction and mixing. Separation processes are thus not included.

## 2.2 Variables Included in the Definition of the Attainable Region

Suppose we have a system of  $n$  species  $A_1 \dots A_n$ , with a specified set of  $r$  reactions:

$$\sum_{i=1}^n \nu_{ij} A_i = 0 \quad j = 1 \dots r \quad (2.1)$$

where the rate of formation of species  $A_i$  is given by  $r_i$ , which depends on the concentrations of the species  $c_i$  and the temperature  $T$ . In order to simplify the notation we will write these arrays of quantities as vectors, thus:

$$\underline{r} = (r_1, r_2, \dots, r_n)$$

$$\underline{c} = (c_1, c_2, \dots, c_n)$$

In particular

$$\underline{r} = \underline{r}(\underline{c}, T)$$

Now let us suppose we are given a specified mass-flow  $M$  of material with reference concentration  $\underline{c}^\circ$ , enthalpy per mass  $\hat{H}^\circ$ , density  $\rho^\circ$  and temperature  $T^\circ$  (for instance a feed condition). It is from this initial material that we wish to determine what final conditions (for example concentration, temperature and residence time) we can achieve in arbitrary systems of reactors using only the processes of reaction and mixing.

We will find it convenient to define variables with units corresponding to concentration, time and temperature respectively. The quantities are defined so that they all obey linear mixing laws and so that changes in them due to reaction may be described by a rate equation. The variables, in fact, simplify to concentration and temperature in certain circumstances. This point will be clarified later.



Let the mass fraction of species  $i$  in a mixture be  $w_i$  and its molecular mass  $m_i$ . We define  $v$  as the total volume of the reactor system. Then:

$$d_i = \frac{w_i \rho^\circ}{m_i} \quad i = 1 \dots n \quad (2.2)$$

$$\text{and } \tau = \frac{v \rho^\circ}{M} \quad \text{the space time} \quad (2.3)$$

$$\text{and } \theta = \frac{\hat{H}}{\hat{C}_p^\circ} \quad (2.4)$$

where  $\hat{C}_p^\circ$  is heat capacity at constant pressure per unit mass at the reference conditions. If the density of the mixture does not change with reaction and mixing, then  $\rho = \rho^\circ$  and  $d_i$  and  $\tau$  become the true concentrations and mean residence time of the system respectively.

The enthalpy of a mixture at constant pressure is a function of the temperature  $T$  and composition and can be written as:

$$\hat{C}_p^\circ \theta = \int_{T^\circ}^T \hat{C}_p^\circ dT + \sum \frac{d_i m_i}{\rho^\circ} \hat{H}_{fi}^\circ + \hat{\Delta H}_m \quad (2.4a)$$

where  $H_{fi}^\circ$  is the specific enthalpy (per unit mass) of formation of species  $i$  at the reference conditions and  $\hat{\Delta H}_m$  is the specific enthalpy of mixing.

If the heat capacity of the mixture does not change with reaction, mixing and temperature then  $\hat{C}_p^\circ = \hat{C}_p$  and the above equation becomes:

$$\theta = (T - T^\circ) + \frac{\sum d_i m_i \hat{H}_{fi}^\circ}{\hat{C}_p^\circ \rho^\circ} + \frac{\hat{\Delta H}_m}{\hat{C}_p^\circ} \quad (2.4b)$$

In this case the quantity  $\theta$  is thus linearly dependent on the change in temperature of a system of constant composition.

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The usual variables which appear in the rate of formation expression  $r_i$  and reactor equations are concentration, residence time and temperature and are related to these new variables as follows:

$$c_i = \frac{\rho}{\rho^0} d_i \quad i = 1 \dots n \quad (2.5a)$$

$$t = \frac{\rho}{\rho^0} \tau = \text{residence time} \quad (2.5b)$$

$$T - T^0 = \frac{\hat{C}_p^0}{\hat{C}_p \text{ mean}} \theta - \frac{\sum d_i m_i \hat{H}_{fi}^0}{\hat{C}_p \text{ mean } \rho^0} - \frac{\Delta H_m}{\hat{C}_p \text{ mean}} \quad (2.5c)$$

where  $\hat{C}_p \text{ mean}$  is the mean value of the specific heat capacity of the mixture, defined as:

$$\hat{C}_p \text{ mean} = \frac{\int_{T^0}^T \hat{C}_p dT}{(T - T^0)} \quad (2.5d)$$

$$\text{and } \rho = \rho(c, T) \quad (2.5e)$$

Let us now join all of the quantities into a single array which we call the characteristic vector  $\underline{C}$  which is a vector with  $(n+2)$  elements ie

$$\underline{C} = (d_1, d_2, \dots, d_n, \tau, \theta) \quad (2.6)$$

We note that the rate of formation vector can be expanded to give us what we can call a reaction vector  $\underline{r}$  such that:

$$\underline{r}(c, T) = (r_1(c, T), r_2(c, T), \dots, r_n(c, T), 1, 0) \quad (2.7)$$

$$\text{or } \underline{R}(\underline{C}) = (R_1(\underline{C}), R_2(\underline{C}), \dots, R_n(\underline{C}), 1, 0) \quad (2.7a)$$

where  $r_i = R_i$  for a given state of the system. Note however that  $r_i$  and  $R_i$  are different functions as they have different independent variables. Thus we will usually refer to  $r_i$  if we

refer to the value of the rate of formation of  $i$  at specified conditions but be more precise and specify either  $r_i$  or  $R_i$  in situations where the functional form is important, such as when integrating or differentiating the rate expression. Note also that the rate expression above implies that reaction is adiabatic.

The reason for using these particular variables  $C$  is that firstly, they each obey a linear mixing rule (discussed later in section 2.3.2) and secondly, the change in the quantity due to reaction can be written in terms of a rate of reaction. We may include any other variables that obey the linear mixing law and where changes in the variable, due to reaction, may be written in terms of a rate of reaction. Thus pressure, for example, cannot be included as a variable, unless somehow it is combined with other variables such that the new variable obeys both constraints. Thus all systems considered in this thesis are constant pressure systems.

We have now set up the basis for the system we wish to discuss.

We note that if we have an isothermal system we merely decrease the size of our characteristic vector by leaving out the final element  $\theta$  as the system will then be a function of composition ( $d_i$ ) and space time ( $\tau$ ) only. Furthermore notice that by leaving the element  $\theta$  out, we are no longer constraining the reaction process to be adiabatic. Thus if the process is isothermal, for example, the rates of formation and density must be calculated at the temperature of the system so that the modified reaction vector will describe an isothermal reaction process.

An adiabatic system with a single feed has a fixed enthalpy. The attainable region for this adiabatic system will consequently be in a subspace of the total space, even though the temperature of the system may vary. The smallest dimension of the space that we can work in, is in this case reduced by one.

Furthermore, we will always include fewer concentration variables in our characteristic vector than found in the stoichiometric space. As discussed by Feinberg (1980), the mass balance constraints confine us to the stoichiometric subspace of the full

concentration space. This subspace is a linear subspace of the full space. The convexity properties that will be shown to be important in our later work depend on points being independent, which is clearly not the case if one is working in either the full concentration space or the stoichiometric subspace. Thus the usual approach that has been adopted in doing examples is to only include the variables that are necessary, ie the ones that appear in the reaction vector as well as those that appear in the objective function of an optimization problem.

### 2.3 The Geometry of Reaction and Mixing

As stated earlier, the only processes we will consider are reaction and mixing. We will not consider reaction systems where other processes are occurring, such as mass transfer, heat transfer or separation processes. None the less, a very wide range of reactor systems can be described by the processes of reaction and mixing only. The consequences and geometric interpretation of these two processes will be discussed in more detail below.

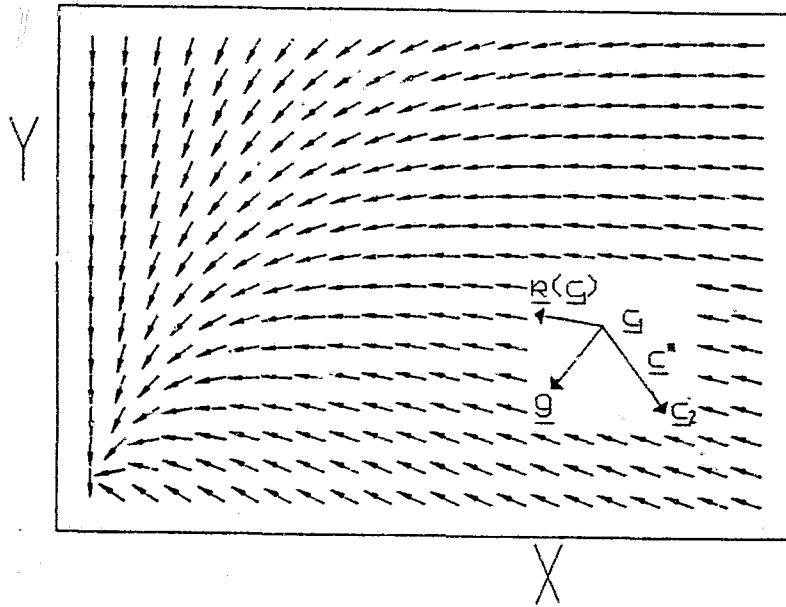
#### 2.3.1 Reaction

We can assign to every point  $\underline{C}$  a reaction vector  $\underline{R}(\underline{C})$ . This vector will have a direction and it is this property of the reaction vector which will prove to be very important. An example showing the the directions of the reaction vector in a two dimensional subspace is shown in Figure 2.1.

If we allow a mixture with properties described by the characteristic vector  $\underline{C}$  to react, the change in the charecteristic vector  $d\underline{C}$  will be described by:

$$d\underline{C} = \underline{R}(\underline{C}) d\phi \quad (2.8)$$

Figure 2.1: The Reaction Vector and Mixing in Concentration Space



where  $\phi$  is a positive scalar quantity with units of time. For simplicity we will usually take the scalar quantity to be the space time  $\tau$ .

Geometrically the reaction vector indicates the direction of change of the characteristic vector due to reaction alone. Notice how the last two components of the reaction vector, that is the time and enthalpy variables, are constant. This will lead to some interesting consequences.

### 2.3.2 Mixing

The elements of the characteristic vector all obey the mixing rule, that is, if we have two streams with mass flow rate  $M_1$  and  $M_2$  and characteristic vector  $C_1$  and  $C_2$  respectively and mix them, then after mixing we have  $C^*$  where:

$$\underline{C}^* = \alpha \underline{C}_1 + (1-\alpha) \underline{C}_2, \quad 0 \leq \alpha \leq 1 \quad (2.9)$$

$$\text{where } \alpha = \frac{M_1}{M_1 + M_2} \quad (2.9a)$$

and  $M_i$  is the mass flow rate of stream  $i$  flowing out of a reactor of volume  $v_i$ .

In particular this is true as:

$$\tau^* = \frac{M_1 \tau_1 + M_2 \tau_2}{M_1 + M_2} \rho^o \quad (2.9b)$$

$$\text{and } \theta^* = \frac{M_1 \hat{H}_1 + M_2 \hat{H}_2}{(M_1 + M_2) \hat{C}_p^o} \quad (2.9c)$$

$$\text{and } d_i^* = \left[ \frac{M_1 w_{i1} + M_2 w_{i2}}{M_1 + M_2} \right] \frac{\rho^o}{m_i} \quad (2.9d)$$

Geometrically, this means that if we mix material described by characteristic vector  $\underline{C}_1$  with material described by characteristic vector  $\underline{C}_2$ , the characteristic vector of the resulting mixture will lie on the straight line joining  $\underline{C}_1$  and  $\underline{C}_2$  (ie inside a convex hull containing  $\underline{C}_1$  and  $\underline{C}_2$ ). Alternatively, the change in concentration of material described by characteristic vector  $\underline{C}_1$  when mixed with material described by characteristic vector  $\underline{C}_2$  is in the direction of vector  $(\underline{C}_2 - \underline{C}_1)$ .

As discussed, we limit ourselves to two processes which can alter our characteristic vector  $\underline{C}$ ; these are mixing and reaction. Mixing  $\underline{C}_1$  with  $\underline{C}_2$  is characterized by a vector given by equation (2.9) and is in the direction of  $(\underline{C}_2 - \underline{C}_1)$  while reaction of  $\underline{C}_1$  is characterized by the vector  $\underline{R}(\underline{C}_1)$  as in equation (2.3). Provided there are no discontinuities, our characteristic vector  $\underline{C}_1$  must change locally in a direction given by the resultant vector:

$$\underline{g} = \beta \underline{R}(C_1) + (1 - \beta)(C_2 - C_1) \quad 0 \leq \beta \leq 1 \quad (2.10)$$

The important conclusion from this is that locally no combination of mixing and reaction can take us in a direction that does not lie between the mixing and reaction vector (ie in the smaller angle between  $\underline{R}(C_1)$  and  $(C_2 - C_1)$ ). Furthermore, this change must lie in the plane defined by the reaction and mixing vector. Figure 2.1 illustrates this idea with an example in two dimensional space. If the reaction and mixing vectors are collinear, then any combination of reaction and mixing will result in a change in concentration along the line defined by equation (2.10).

RESULT 1

RESULT 2

#### 2.4 Definition of the Attainable Region

We define the attainable region as the region in the space of the characteristic vector  $\underline{C}$  which can be reached by any possible (physically realisable) reactor system from a given feed. The feed need not be a single point in the space but could be represented by any number of characteristic vectors, for example the feed material could have a whole range of inlet temperatures. Generally a single feed point will be denoted  $\underline{C}_f^{\circ}$ , whereas a range of feed points will be denoted by the set  $\{\underline{C}_f\}$ .

Now the equilibrium point(s) is never strictly attained as it is only reached as a limit as  $\tau$  tends to infinity. In order to overcome this difficulty we will expand the above definition to include all the limit points (that is boundaries) as well. This makes the attainable region a closed set and does away with some of the difficulties in handling the existence of open sets. Thus we include the limit of  $\tau$  as  $\tau$  tends to infinity in the set as well as the equilibrium concentrations and enthalpy.

Furthermore if we mix any finite point in the space with a sequence of points which tend to the equilibrium point(s), we obtain a line which tends to a "vertical" (ie parallel to the time axis) line. This "vertical" line is strictly not attainable but again we allow it as a limiting process. If

these "vertical" lines form part of the boundary then we have points on the boundary which represent the same concentrations with different times which is clearly not possible, but we will still accept these "vertical" lines as the boundary of the region, thus closing the set.

#### 2.4.1 The Constrained Attainable Region

An interesting and useful offspring of the attainable region is the constrained attainable region, defined as the region in the space of the characteristic vector that can be reached by using only a specified number and type of reactors - for example, three plug flow reactors. It is interesting to note that the ideas developed for the attainable region can be applied to the constrained attainable region. It turns out for many examples, the constrained attainable region is equivalent to a geometric optimization relative to a given reactor structure and that results can be found in cases where traditional optimization techniques can not or have not been used. Examples will be done in Chapters 3 and 4 to show the usefulness of this concept.

#### 2.5 The Existence and Uniqueness of the Attainable Region

Define the base of the attainable region as the closure of convex hull of the feed point(s) and the equilibrium point(s). We note that as a result of our closure of the set these points are all attainable. (We reiterate that we do not allow sustained oscillations). The result is that the base is attainable and as it is non-empty and attainable, the existence of the attainable region is assured.

Once the difficulty of the limit point(s) has been cleared up, the proof of the uniqueness follows fairly easily. This is because infinities exist only in the time domain while the concentration and enthalpy space are bounded.



Furthermore, as its name implies, this base must always be the foundation on which any attainable region rests (for arbitrary kinetics). Suppose for the given kinetics we find two distinct attainable sets R and S on this base U, then using mixing the convex hull of the union of R and S is attainable. This process can be repeated for any finite sequence of such sets.

For an infinite collection of such sets we can perform the same sequence of operations and, as either the space is bounded (as for concentrations) or as we have included the limit as  $\tau \rightarrow \infty$ , such processes must have limits. Then, provided we allow the limit points to be part of the region, by the process of taking convex hulls of unions of sets we will arrive at a single non-empty set. We have thus proved the existence and the uniqueness of the attainable region. We may further note that because of the construction method of taking the convex hull of the unions of sets the attainable region must be a compact, simply connected region and in particular must be convex.

RESULT 3

## 2.6 The Geometry of Some Idealized Reactors

Assume that the reference conditions are the feed conditions.

### 2.6.1 The Plug Flow Reactor

The plug flow reactor has as its defining equation:

$$\frac{dC}{d\tau} = \underline{R}(C) \quad \underline{C}(\tau^0) = \underline{C}_f \quad (2.11)$$

The plug flow curve is thus a trajectory in the space such that the reaction vector is tangent to the curve at each point. These trajectories are uniquely determined by their initial points on the boundary of the region and cannot cross each other. We can

RESULT 4

envisage the space to be completely filled by these curves. In particular, because  $\tau$  does not occur explicitly in the vector field  $\underline{R}(\underline{C})$ , the trajectories starting from different initial times but with the other initial values the same, are just the same curves but shifted up or down the time axis.

RESULT 5

2.6.2 The Continuously Stirred Tank Reactor or the C.S.T.R.

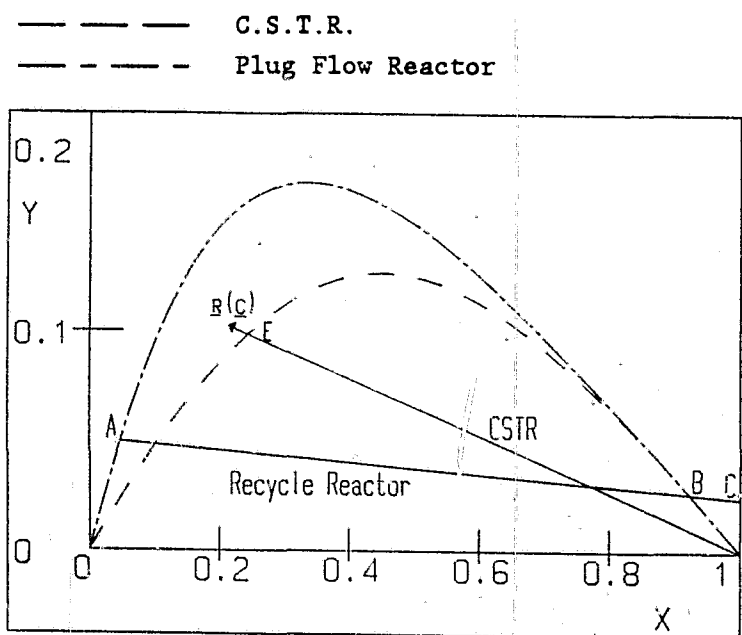
The C.S.T.R. has the defining equation:

$$\underline{C} - \underline{C}_f = \underline{R}(\underline{C})(\tau - \tau^0) \quad \underline{C}(\tau^0) = \underline{C}_f \quad (2.12)$$

The C.S.T.R. has the property that, for each  $(\tau - \tau^0)$ , the vector defined as the difference between the feed and exit concentrations  $\underline{C}$  is collinear with the reaction vector at the exit conditions. A diagram of the locus of all such points, with  $(\tau - \tau^0)$  as a parameter, in a two dimensional space is shown in Figure 2.2.

RESULT 6

Figure 2.2: The Plug Flow, C.S.T.R. and Recycle Reactors



Note that all points along DE are possible feed points to a C.S.T.R. with exit concentration E. However the locus, although it may not always be single valued, is unique to a C.S.T.R. with feed concentration D.

### 2.6.3 The Recycle Reactor

The recycle reactor is a plug flow reactor but some of the exit material is recycled to the inlet. It is defined by the following equations:

$$\frac{dC}{d\varphi} = \frac{R(C)}{(R+1)} \quad \begin{aligned} C(\varphi=0) &= C^* \\ C(\varphi = \tau - \tau^0) &= C^{\text{ex}} \end{aligned} \quad (2.13a)$$

$$C^* = \frac{RC^{\text{ex}} + C_f^0}{R + 1} \quad (2.13b)$$

where  $R$  is the recycle ratio, that is the mass flow rate ratio of the recycle flow rate to the feed rate;  $C^{\text{ex}}$  is the exit concentration of the recycle reactor and therefore the plug flow reactor and  $(\tau - \tau^0)$  corresponds to the space time of the recycle reactor. The recycle reactor is a plug flow reactor with a feed at a weighted average between the exit concentration  $C^{\text{ex}}$  and the given feed  $C_f^0$ . The variable  $\varphi$  is an independent, scalar quantity related to the space time of the material in the plug flow section of the reactor. The geometric interpretation is shown for a two dimensional example in Figure 2.2. It can be seen that when the recycle ratio tends to zero, we tend to a plug flow and when the recycle ratio tends to infinity, we tend to a C.S.T.R. The recycle ratio can be geometrically interpreted as the ratio of distance BC to AB.

RESULT 7

Notice that by varying the recycle ratio  $R$ , any point on BC could be a feed point to a recycle reactor with exit concentration A. The locus shown is for a fixed recycle ratio and feed concentration.

## 2.7 Necessary Condition for the Attainable Region

The necessary condition will first be stated and proved. Thereafter, all the results that arise from this condition will be discussed. The question of which other conditions are needed in order to complete the sufficiency condition will be discussed and it will be shown that the main deficiency in the condition is related to incomplete information concerning multiplicity of solutions in reactors.

### 2.7.1 The Necessary Condition

We can write the following necessary condition for the attainable region.

It is necessary that the attainable region  $A$  on its base with feed concentration  $(C_f)$  is such that:

- (a) it is convex.
- (b) no reaction vector in the boundary of  $A$  ( $\partial A$ ) points outward from  $A$ ; that is all reaction vectors in  $\partial A$  point inwards, are tangent to  $\partial A$  or are zero.
- (c) there is no plug flow trajectory in the complement of  $A$  (within the stoichiometric subspace) which has two points such that the line joining the later point to the earlier point can be extended to intersect  $\partial A$  (and hence  $A$ ).
- (d) no negative of a reaction vector in the complement of  $A$  (within the stoichiometric subspace), when extended can intersect a point of  $\partial A$  (and hence  $A$ ).

2.7.2 Proof of the Necessary Condition

Each of the conditions correspond to operations associated with mixing or to one of the reactors we have examined in the previous section. We will prove the condition by contradiction. Assume  $A$  is the attainable region and let us examine each of the cases in turn:

(a') Suppose  $A$  is not convex. By using the operation of mixing we may attain any point in the convex hull of  $A$ . Some of these points will be strictly in the complement of  $A$ . But this contradicts our assumption that  $A$  was the attainable region. Thus because of mixing,  $A$  must be convex.

(b') Suppose a non-zero reaction vector on  $\partial A$  points outwards at some point  $P$  then we could by using the appropriate plug flow trajectory starting at  $P$  attain the complement of  $A$ . Thus (b) must be satisfied.

One can note that if there is a continuous section on the boundary where the reaction vector is tangent to the boundary, this will be part of a plug flow trajectory. Obviously if the reaction vector is zero on the boundary we are talking about an equilibrium point.

(c') Suppose (c) is false then a recycle reactor could be used to extend  $A$ . The fresh feed point would be a point in  $A$  (or on  $\partial A$ ) which is intersected by the extended line. The mixed composition would correspond to the earlier point and the outlet composition would be the later point on the plug flow trajectory. Thus (c) must be true.

(d') If (d) is false, then starting from a point in  $A$  (or  $\partial A$ ) a C.S.T.R. could be used to reach the point in the complement of  $A$  where the negative of the reaction vector originates. This proves (d) which it should be noted is the limit of condition (c) as the two points on the plug flow trajectory approach each other.

## 2.7.3 Further Properties of the Attainable Region

At present there is only a necessary condition for the attainable region. In order to complete the analysis one would need a sufficiency condition or show that a region satisfying the necessary condition is unique.

When we do examples, in order to ensure that we do not obtain regions which satisfy the necessary conditions but are not attainable, we will construct the region using only points we know are attainable. In this way, even though we do not ensure that we have the full attainable region itself, the region we obtain, that satisfies the necessary condition, will be attainable.

It is clear that an attainable region which we have constructed that satisfies the necessary condition cannot be extended by the processes of mixing, a plug flow reactor, a recycle reactor or a C.S.T.R. This follows from the following reasoning.

RESULT 8

Suppose  $A$  is an attainable region based on  $(C_f^0)$  and which satisfies the necessary condition. Let  $B$  be a region based on  $(C_f^0)$  constructed only using the processes of mixing, the plug flow reactor, the recycle reactor and the C.S.T.R., but  $B \not\subset A$  and is not completely contained in  $A$ . Let us look at that piece of  $B$  that does not contain the intersection of  $A$  and  $B$  (that is  $A \cap B$ ). Now points in  $A$  are attainable,  $A$  is convex and includes the base. However, points in  $B/A (= B - A \cap B)$  are attainable from  $A$  since they are attainable from the base which is in  $A \cap B$ . Thus there must be at least one plug flow reactor, one recycle reactor or one C.S.T.R. with a feed point in  $A$  and a product point in  $B/A$ . But the boundary surface separating  $A \cap B$  and  $B/A$  consists of points in  $\partial A$ . Thus one of the conditions (b) (c) or (d) is violated on that portion of  $\partial A$ . Hence if (a), (b), (c) and (d) are true  $A$  cannot be extended using the four processes.

Furthermore if a recycle reactor forms part of the boundary we can always achieve those boundary points by a plug flow reactor starting from inside the attainable region. This can be shown as follows.

RESULT 9

Let us now look at recycle reactors. Suppose we have a region which obeys the necessary conditions and suppose that the outlet concentration of a recycle reactor lay on the boundary of the region. There are four possibilities for the final plug flow section:

(i) the plug flow at the end of the recycle reactor points out of the region. This contradicts (b) of the necessary condition.

(ii) the plug flow at the end of the recycle reactor points into the region. In order for the feed point of this plug flow reactor to be inside the region, the plug flow trajectory must have left the region at another point again contradicting (b) of the necessary condition.

(iii) The plug flow at the end of the recycle reactor is entirely in the boundary of the region. The convexity requirements of (a) ensures the feed point of the recycle reactor is external to the region.

(iv) The plug flow at the end of the recycle reactor is in the boundary but comes from inside the region. (It cannot start outside the region and move into the boundary as the feed point would need to be external to the region). In this case a valid feed point from inside the region would result in a boundary point which is the exit point of a recycle reactor. However as the plug flow reactor starts inside the attainable region we can always achieve this boundary point from a feed point inside the region using a plug flow alone.

This proves our assertion.

This limited sufficiency result leaves open the question of whether we could expand the attainable region by any other processes. It is easy to see that any differential process involving reaction and mixing cannot be used as the result

expressed in equation (2.10) precludes this. Similarly any series-parallel arrangement of the idealized reactors or indeed any simple reactor that involves processes of differential mixing and reaction cannot extend the region. This can be shown as follows: If the individual reactors start in the attainable region, they cannot move out of the attainable region. Reactors in series cannot therefore extend the region. A parallel arrangement of reactors is equivalent to mixing the outlet material from the individual reactors. This is described by the mixing rule, and the characteristic vector of the resulting material must, due to the convexity property of the region, also lie in the attainable region. Any series-parallel arrangement of reactors, by the same argument, can also not extend the region.

RESULT 10

RESULT 11

This however does not exclude other more complex reactors where a concentration jump can occur. Such cases could be the axial mixing reactor or a series of simple reactors with complex recycles. In all of these reactors there are jumps in concentration, such as occur in the recycle reactor and the C.S.T.R., and we are not sure whether such a reactor can extend the region we have constructed using the conditions (a), (b), (c) and (d). The jump condition that causes the difficulty is that relating to multiple steady states where a new solution may appear in a different part of the space as one follows the locus of the reactor.

This will be explained by means of an example - the recycle reactor. The family of main branches of the loci will be smooth curves starting at the feed point (ie in the limit as  $\tau \rightarrow 0$  the outlet concentration will tend to the feed concentration for all values of the recycle reactor). Each curve will correspond to a different recycle ratio. In the case where the recycle reactor does not exhibit multiple steady states, these curves will move from the feed point to the equilibrium point(s) and, as the recycle ratio increases, the curves will move away from the plug flow trajectory towards the locus of the C.S.T.R. In the limit, as the recycle ratio tends to infinity, the curve will coincide with that of the C.S.T.R. locus. An interesting result is that the main branch of the recycle reactor, with a feed point inside a region that satisfies necessary conditions (a) and (b) cannot leave the region. The main branch refers to the locus which

RESULT 12



starts at the feed point and which continues smoothly to the equilibrium point. The proof of this is discussed in Theorem 2.1 in Section 2.10. Condition (c) is thus not needed for these cases and the attainable region could very well have been constructed using only conditions (a), (b) and (d).

Consider the case where the recycle reactor does exhibit multiple steady states. Branches of the recycle reactor locus that approach a C.S.T.R. solution as the recycle ratio tends to infinity would have been included in the construction of the attainable region. Branches that might not have been included in the construction of the attainable region when using only conditions (a), (b) and (d) are those that arise and which do not map into the C.S.T.R. locus as the recycle ratio is changed. These would be branches of the solution that exist for only certain values of the recycle ratio and which are not connected to other branches that approach the C.S.T.R. limit. In other words, the following question arises: can the solution of recycle reactor exhibit more branches than the C.S.T.R.? The answer to this question does not seem to be known. From the geometric interpretation of the recycle reactor, it would seem that one would need fairly pathological kinetics for this to happen (see Section 2.10). However, the important conclusion is that condition (c) is only needed to cover this possibility. Thus if the recycle reactor cannot exhibit more branches than the C.S.T.R., condition (c) of the necessary condition is not needed.

RESULT 13

Another interesting result is that a system consisting of a series-parallel arrangement of recycle reactors, although it has more solutions than than a single recycle reactor, does not introduce new solutions that must be covered by a necessary condition in that all solutions must be combinations of the steady states of a single recycle reactor. Thus all the multiple steady states of any series-parallel combinations of a simple reactor are just convex combinations of the steady states of that simple reactor. The necessary condition would therefore, provided the steady states of the simple reactor were covered, also cover the series-parallel combinations of the simple reactor.

RESULT 14

A complexity is introduced if one however allows back mixing ie allows a recycle over more than one reactor. We know in the limit as the residence time tends to zero the solution must approach the feed point. As the residence time increases there must be a locus from the feed point and this would lie inside the attainable region. (In order that the locus cross the boundary of the attainable region, at some point one must have a reaction vector moving out of the attainable region, which is clearly not possible. The argument is analogous to that for the recycle reactor, and is discussed in Section 2.10). Thus only branches that started outside the attainable region have not been included in our condition. Thus it is only where multiple solutions are exhibited that the sufficiency condition is deficient.

RESULT 15

This result pointed to the importance of multiplicities of reactors, and although we have not been able to prove any results that could provide further necessary conditions or a sufficiency condition, other interesting results have been found.

#### 2.7.4 Multiple Steady States

The full proofs of the following results are given in Appendix 1. A summary of the results and a discussion of the importance of these results is given below.

The Maximum Mixedness Reactor Model (MMR) can only exhibit multiple steady states for systems where the residence time distribution tends to infinity.

RESULT 16

This arises because multiplicity cannot be introduced by:

- sections of reactor where the side material is introduced in a smooth continuous manner
- any points where a finite amount of material is added in the side stream as mixing does not introduce any multiplicities.
- the initial point if a finite amount of material is added. If the beginning of the reactor has this configuration, the reactor

will have a finite upper bound on the residence time distribution.

The multiplicity must either arise from the initial point or because the concentration along the reactor with respect to remaining life does not tend to a limit (for example, the concentration may vary periodically). Behaviour of this type was discussed by Glasser et al (1986). If the multiplicity arises from the initial point, this point must satisfy the C.S.T.R. equation. Thus geometrically the reactor with feed  $C_f^0$  can be interpreted as follows: the MMR would start at some point on the C.S.T.R. locus, say  $C$ , which corresponds to a solution of the C.S.T.R. having feed point  $C_f^0$ . The trajectory would then move in the direction between the reaction vector and the mixing vector ( $C_f^0 - C$ ) and this section of the reactor would be a smooth curve if the side stream is added smoothly and continuously. At points where a finite amount of feed was added, the curve of the MMR would have a discontinuity in that it would move a finite distance along the mixing vector. Neither of these processes would introduce multiplicities, and thus this type of reactor would lie inside the attainable region as defined by necessary conditions (a), (b) and (d).

RESULT 17

RESULT 18

Unfortunately the same cannot be said as yet for reactors that do not tend to a limit. An approach that might lead to something fruitful is the following: A recycle reactor exhibits periodicity, the periodicity depending on the residence time and the recycle ratio. We might be able to show that the sum of recycle reactors could approximate the periodic behaviour of any other MMR ie use ideas similar to Fourier series. Whether this could approximate any periodic variation in concentration is not known, but it might be a useful suggestion.

Reactors that can be described by the General Mixing Model (GMM) of Jackson and Glasser (1984) will either:

- exhibit branches that arise because the concentration along the reactor with respect to remaining life does not tend to a limit.
- lie inside the region satisfied by necessary conditions (a), (b) and (d).

RESULT 19

The mixing that occurs in the GMM does not in general cause multiple solutions. The only multiplicities that may arise are by elements of fluid behaving as C.S.T.R.'s or because the concentration with respect to remaining life along the reactor does not tend to a limit. If the multiplicities arise from the first cause, these reactors will satisfy the necessary conditions (a), (b) and (d), ie they will lie inside the region satisfying these conditions as explained above.

Further work is required to understand reactors where the concentration along the reactor with respect to remaining life does not tend to a limit. An example of this type of behaviour is the recycle reactor, where the concentration varies periodically with respect to remaining life.

Thus in summary, the multiple solutions which are not covered by the necessary condition are those resulting when the concentration with respect to remaining life does not tend to a limit. When the nature of this behaviour is better understood, the necessary condition could be expanded to include these.

## 2.8 The Sufficiency Condition

It would seem that the only deficiency in the sufficiency condition relates to the number of multiplicities of solutions for reactors. In particular, the reactors where the concentration with respect to remaining life does not tend to a limit, when one regards them in terms of the MMR or GMM, may not be covered by the necessary condition. The important question that must be answered is this: are there reactors which have solutions which either do not map into those of the C.S.T.R. or recycle reactor via differential processes or which are not convex combinations of the solutions of the C.S.T.R. or recycle reactor. If this is not possible then the above necessary condition would appear to be sufficient. Another interesting result is that condition (c) is not needed if all branches of the recycle reactor map into the C.S.T.R. The necessary condition, as given

in Section 2.7.1, covers a very large class of reactors. These include all single and parallel-series arrangements of plug flow reactors, C.S.T.R.'s, recycle reactors, any other reactor in which differential mixing and reaction occurs and finally any steady flow reactor which has a bounded residence time distribution. The missing results regarding the behaviour of the multiple solutions of reactors certainly opens an interesting area of research.

## 2.9 The Construction of the Attainable Region

In order to find the attainable region, we must find a region that both satisfies the necessary condition and that is indeed attainable. We therefore use a construction method, in which we start with the feed point(s) and use the processes of reaction and mixing, to find an attainable region that satisfies the necessary condition. As discussed above, we may be able to extend the region using complex reactors that exhibit multiple steady states, but the region which we find by the construction method is at least attainable. The construction method will vary depending on the exact nature of the problem and the imposed constraints, but it will always more or less follow the following sequence:

- construct the plug flow trajectory(s) from the feed point(s). Find the convex hull of the trajectory(s), which is equivalent to finding all the points that are achievable by mixing all the possible outlet materials of the plug flow reactor(s) in all combinations.
- check whether any reaction vectors point outwards on the boundary of the hull.
- if reaction vectors point outwards, then find the best feed point and, if unconstrained, type of reactor that will extend the region the most. Be sure to include all possible branches of the reactor curve if applicable. Find the new convex hull and repeat step 2.

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- if no reaction vectors point outwards, check whether necessary conditions (c) and (d) are met. If they are not met, extend the region using the appropriate reactor which is exhibiting the multiple steady states, find the new convex hull and repeat from step 2.

- if the necessary condition is met, we have a region that satisfies all the conditions and which is achievable. This region is then a candidate for the attainable region.

Thus by following this method, we can construct an attainable region for any set of reactions. The construction method is particularly easy to apply in two dimensions but the ideas can be used to find the attainable region in any number of dimensions.

### 2.10 Discussion of Chapter 2

**THEOREM 2.1 :** Given a region A that satisfies the following conditions:

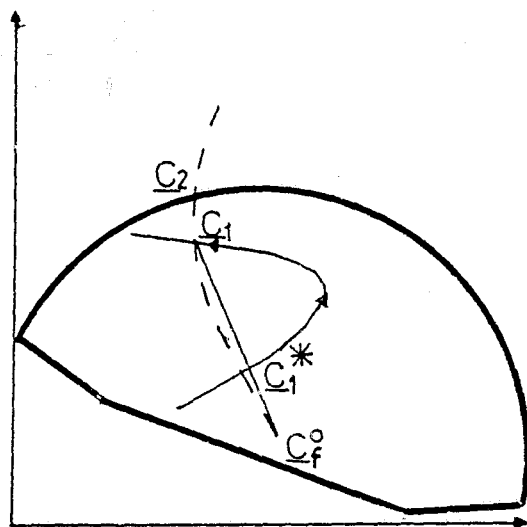
- it is convex;
- no reaction vectors on the boundary of A point outwards from A, ie all reaction vectors are tangential, point inwards or are zero;

a locus of a recycle plug flow reactor with fixed recycle ratio  $R$  that starts inside the region A, and that is continuous in residence time  $\tau$ , cannot leave A. By continuous in residence time, we mean that a small change in residence time results in a small unique change in concentration. (This excludes other branches of the recycle reactor.)

**PROOF:** Consider a recycle reactor for a fixed recycle ratio that leaves the region A at  $C_2$  as shown in Figure 2.3. The starting concentration of the locus  $C_f$ , represents the feed to the recycle reactor. Each point on the locus, for example  $C_1$ ,

Figure 2.3: Figure for Proof that Recycle Reactor Locus Cannot Extend a Region that Satisfies Conditions of Theorem 2.1

————— Boundary of Attainable Region A  
 - - - - - Recycle Reactor Locus  
 ————— Plug Flow Trajectory



represents the exit concentration of the recycle reactor at some residence time  $\tau_1$  and with the given recycle ratio  $R$ . Thus there is a plug flow reactor with some feed  $C_1^*$  and a residence time  $\tau_1/(R+1)$  that has an exit concentration  $C_1$ . The feed concentration  $C_1^*$  must lie on the straight line between  $C_1$  and  $C_f$  and the exact position will be determined by the value of the recycle ratio. The feed concentration must always lie inside the region as both  $C_1$  and  $C_f$  lie inside the region and the region is convex.

Now consider the plug flow reactor that gives rise to the exit concentration  $C_2$  on the boundary of A. The recycle reactor will have some residence time  $\tau_2$ ; and the feed to the plug flow reactor section,  $C_2^*$ , must again lie on the line joining  $C_2$  and  $C_f$  and must lie inside A as A is convex.

If we were to increase the residence time of the reactor by  $d\tau$ , then the exit concentration will also change by a differential amount. However, the new concentration cannot lie outside the

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region A as this would mean some plug flow reactor (in the neighbourhood of the plug flow reactor with feed  $C_2^*$ ) starting inside the region had crossed the boundary of A which is not possible if the reaction vectors on the boundary do not point outwards.

**CONJECTURE 2.1 :** It is not generally possible for the recycle reactor to have branches that do not either tend to the C.S.T.R. limit or that are not connected to branches that tend to the C.S.T.R. limit.

**DISCUSSION:** Consider a branch of a recycle reactor that has feed point  $C_f$  and that ends by not approaching the limit of a C.S.T.R., or in other words, it exists for only certain values of the recycle ratio. Consider how this branch begins and ends. It could either be an open or a closed curve.

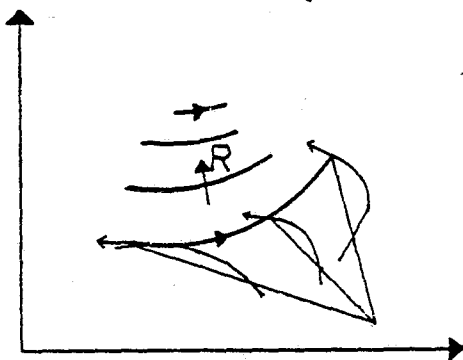
Consider the first option: an open curve. This would require that somewhere the recycle reactor locus suddenly begins; and that along this locus we have a family of plug flow trajectories that satisfy necessary condition (c). Thus if we start at the first point on the locus, and the associated plug flow trajectory, we find that when we move to a neighbouring point on the locus, we also move to a neighbouring plug flow trajectory that also satisfies necessary condition (c). Moving along the locus is equivalent to changing the residence time of the recycle reactor. The intersection points of the line from the feed point with the plug flow trajectories will also vary smoothly as one moves to neighbouring curves, ie changes the residence time (see Figure 2.4a). If the resulting locus comes to a sudden end, as in the case of a open curve, this would mean either that, as the residence time was increased, one could not find a neighbouring trajectory that satisfied necessary condition (c), or that one had reached an equilibrium point. We know that the space must be filled with plug flow trajectories and that the trajectories will vary smoothly and continuously in any direction and will not ever intersect. Thus if we have condition (c) that can be satisfied at a point but not by any neighbouring point, as at the beginning



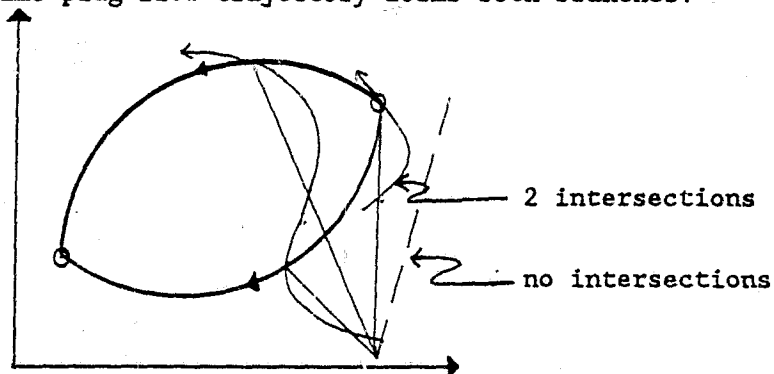
Figure 2.4: Figure for Conjecture that Recycle Reactor Locus Cannot Have More Branches than the C.S.T.R.

\_\_\_\_\_ Recycle Reactor Loci  
 \_\_\_\_\_ Plug Flow Trajectories  
 o Closure point

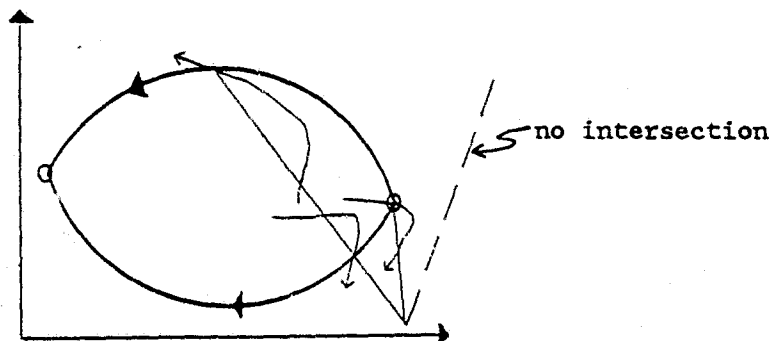
(a) Case 1: The Recycle reactor curves are open curves.



(b) Case 2.1: The Recycle reactor curves are closed curves; the same plug flow trajectory forms both branches.



(c) Case 2.2: The Recycle reactor curves are closed curves; different plug flow trajectories form the branches.



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and end of the branch (if it does not end at an equilibrium point), this would require fairly odd kinetics. But the case when this occurs must be even more peculiar. The branch exists for a range of recycle ratios, and thus there must be a family of end points where necessary condition (c) can not be satisfied by any neighbouring point. Furthermore, the two limit curves, ie the branches with the smallest and largest recycle ratio's, are also such that the condition (c) cannot be met if one changes the recycle ratio slightly. Thus it is suspected that the kinetics that cause the plug flow trajectories to exhibit this odd behaviour, would have to be rather pathological.

Consider the case of a closed curve, that is the second option. At the point where the curve closed, it would require a plug flow trajectory to behave in such a manner that condition (c) was met. As one changed the parameters slightly, for example the residence time, the exit concentrations would change slightly along the curve and away from the closure point. There are two ways in which this might happen:

(i) The same plug flow trajectory may be intersected by two different lines from the feed point  $C_f^0$  ie be intersected four times. However, as one approaches the closure point, it would require that two of the intersections approached closer and closer and eventually disappeared, leaving only two intersections. This would require that, as the two intersection points approached each other, the lines would become collinear and thus that reaction vector to be tangential (see Figure 2.4 b). Thus this would in turn imply that there was a C.S.T.R. limit point in the vicinity. Thus this case would not satisfy the assertion.

(ii) Alternatively the branches could be formed by different plug flow trajectories, ie every plug flow trajectory that makes up a branch is only intersected twice by a line from the feed point  $C_f^0$  (see Figure 2.4 c). Presumably, if the behaviour of the trajectories is similar, then again fairly odd kinetics would be required as, within a very small neighbourhood, one could find two, one (at the closure point) and then no plug flow trajectories that can be intersected by the straight line through the feed point  $C_f^0$ . If one again considers the further

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requirement that this behaviour is required for a range of recycle ratios, and that the closure point for each recycle ratio would presumably vary smoothly with varying recycle ratio's, this too would require extremely odd kinetics.

QUESTION: Can a branch of a recycle reactor go to another equilibrium point that the main branch(s) cannot reach, or that is not bounded by the plug flow or C.S.T.R. equilibrium point(s)?

CONJECTURE 2.2: No main branch of any reactor structure can move outside a region A that satisfies necessary conditions (a), (b) and (d), if the feed point to the reactor lies inside the region.

DISCUSSION: It has been shown that:

- plug flow, C.S.T.R. and recycle reactors cannot extend (ie move out of) a region, such as region A, that satisfies the necessary condition.

- no process of differential mixing and reaction can extend region A (see Result 10).

- no series-parallel arrangement of ideal reactors or reactors with differential mixing and reaction, can extend region A.

- no forward mixing, such as occurs in the MMR or the GMM, can extend the region, if no periodic variation of concentration with remaining life occurs.

Thus the reactors that are not covered by the above results, are those that have complex recycles and those that exhibit a jump condition in concentration, for example the MMR and GMM reactors which exhibit periodic behaviour.

Let us consider the behaviour of the main branches of such reactors. For very small residence times, the exit concentration must approach that of the feed concentration, which by definition lies inside, or on the boundary of, the region. In fact, the

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concentration at all points in the reactor must be very close to that of the feed concentration and, in the limit, approach that of the feed point as the residence time approaches zero. There must always be at least one section of the reactor where reaction occurs, be it in the form of differential reaction, or differential reaction and mixing or reaction and mixing as in the C.S.T.R. For small residence times, this section must move us away from the feed point very slightly.

As the residence time is increased, so the exit concentrations from the reaction section(s) will change smoothly and continuously. An alternative way of thinking of this process is as follows: We consider all the concentrations that are found in the reactor and take the convex hull of all these points. This, for simplicity, we shall call the convex hull of the Reactor. We find that points that form the vertices of the convex hull of the reactor can only be reached with some reaction (ie not mixing only). As the residence time of the reactor is changed, so the boundaries of the convex hull of the reactor must change smoothly and continuously. Eventually as the residence time is increased, a point(s) on the boundary of the convex hull of the reactor will lie on the boundary of the region defined above. This point, or at least one of the points, must be a vertex of the convex hull of the reactor. If the residence time of the reactor is increased further, this point that lies on the boundary of the region defined above will move a small amount. However the movement cannot be across the boundary of the region defined above, as necessary conditions (a), (b) and (c) preclude this. Thus the main branch of any reactor is confined to stay inside the region defined above.

In the following chapter, two dimensional examples will be considered and the general results that arise from the construction of the attainable region in two dimensions will be discussed. In Chapter 4, three dimensional examples will be examined and the general results that apply to three dimensional space will be discussed. Some of the results will be generalised to any n-dimensional space in Chapter 5.

CHAPTER 3

TWO DIMENSIONAL EXAMPLES

3.1 Introduction

In this chapter, examples that can be done in two dimensional space will be discussed. These are cases where the reaction vector and the optimization functions depend on two or less independent variables. Most of the examples given in this chapter have been already described by Glasser et al (1987) and Hildebrandt et al (to be published).

It will shown, how by using the idea of the attainable region, one can construct a region that satisfies the necessary condition and that represents a candidate for all possible outlet conditions for the given kinetics. It will further be shown how this region can be used for solving optimization problems. Examples to find the constrained attainable region, that is all possible outlet conditions that can be achieved when using a number of specified reactors, will be done. This approach has been very successful at finding optimal cold shot cooling and interstage cooled reactors. The method can furthermore be used when the standard optimization results no longer hold.

3.1.1 The Necessary Condition

The following result only applies in two dimensions.

A two dimensional region A; that satisfies necessary condition (a), (b) and (d); cannot have a branch of a recycle reactor locus that lies outside of A if the feed point to the reactor lay inside A.

RESULT 20

Alternatively, in two dimensions, necessary condition (c) is already covered by necessary condition (d).

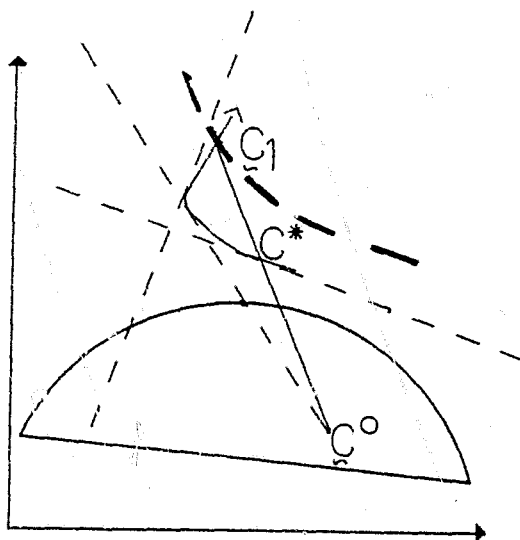
PROOF: Suppose a branch of a recycle reactor locus with feed concentration  $C^*$ , which lies inside A, lay outside of A as shown in Figure 3.1. Note that region A satisfies necessary condition (a), (b) and (d).

Consider point  $C_1$  on the recycle reactor locus. There is a plug flow reactor trajectory from some point on line  $(C^*, C_1)$ , say  $C^*$ , that passes through  $C_1$ .

The reaction vectors along the plug flow trajectory are tangent to the curve. The slope of these reaction vectors will vary continuously along the curve (or in the case of the plug flow

Figure 3.1: Figure for Proof of Result 20

- Boundary of the Attainable Region
- - - - - Branch of Recycle Reactor Locus
- Plug Flow Trajectory



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trajectory lying on line  $(C^*, C_1)$ , be equal to the slope of the line). The slope of the reaction vector will vary from greater to less than that of line  $(C^*, C_1)$ .

When the reaction vectors are projected backwards towards region A, a set of lines with different slopes are produced. By the Mean Value Theorem there will always be at least one reaction vector that when extended back will pass through  $C^*$ . This reaction vector will also be a solution of a C.S.T.R. with feed in A and thus our condition of all the C.S.T.R. loci lying in A is not met.

Thus in two dimensional space, the solution of a recycle reactor can only have branches that terminate in a C.S.T.R.

### 3.2 Examples In Concentration Space

#### 3.2.1 Example 1: Van de Vusse Kinetics

The example we begin with is that usually called the van de Vusse example. The previous work that has been done on these kinetics was discussed in section 1.4.1. The van de Vusse reaction network is:



The kinetics of both reactions in (3.1a) are first-order irreversible while that for (3.1b) is second-order irreversible. Thus the rate of formation of A is given by:

$$r_A = -k_1 c_A - k_3 c_A^2 \quad (3.2)$$

and the rate of formation of B is:

$$r_B = k_1 c_A - k_2 c_B \quad (3.3)$$

Suppose that we are interested in an objective function which is a function of the concentrations of A and B only, for instance the maximization of the concentration of B. Using these kinetics and this objective function we can see that we need only work in two dimensions and effectively we have only two independent dimensionless constants which we can define as:

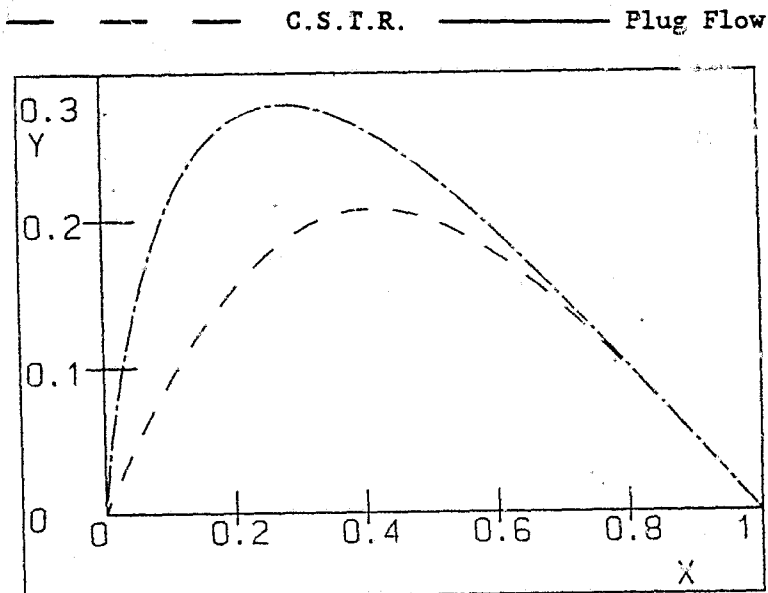
$$a_1 = \frac{k_3 c_A^0}{k_1} \quad \text{and} \quad a_2 = \frac{k_2}{k_1} \quad (3.4)$$

This is true since in concentration space only the relative values of the rate constants matter and not the absolute values. It is only if we were interested in time as well, that the individual values of the rate constants would be important. Let us choose a value of  $a_1 = a_2 = 1$ . Now starting at our feed concentration of:

$$\frac{c_A}{c_A^0} = x = 1 \quad \text{and} \quad \frac{c_B}{c_A^0} = y = 0$$

we can draw the plug flow trajectory on the x-y axes. This trajectory is a convex curve as shown in Figure 3.2. Now let us take the region bounded by this plug flow trajectory and the axis  $1 \geq x \geq 0$ ;  $y = 0$ , (all points on the axis are attainable by mixing feed with the final product and this is our base). This is a convex region with rate vectors tangent to the curve on the plug flow trajectory while on the line  $y = 0$  between  $x = 0$  and  $x = 1$  the rate vectors all point inwards i.e.  $\underline{r} = (-x - a_1 x^2, x)$ . It can readily be seen that no plug flow trajectories in the complement of this region can be made to violate condition (c) and that the C.S.T.R. locus lies entirely within the region. Thus this region satisfies the necessary condition for the attainable region. Using this region the maximum possible concentration of B is attained using a plug flow reactor to the point where  $dy/dx = 0$  and gives a value of  $y = 0.278$ . No better result is possible using mixing, plug flow reactors C.S.T.R.'s or recycle reactors or any series/parallel combination of these but we have not as previously discussed, conclusively shown that this is the best.



Figure 3.2: Van de Vusse Example with  $a_1 = a_2 = 1$ 

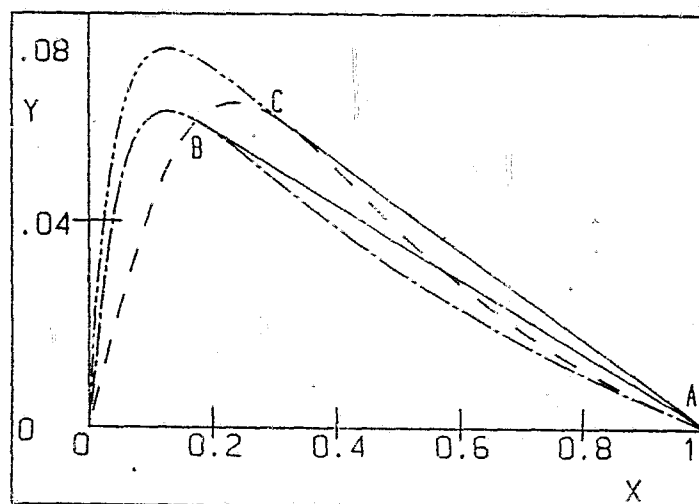
Let us now look at the case where  $a_1 > a_2$  and in particular use values  $a_1 = 20$  and  $a_2 = 2$ . As before we draw the feed plug flow trajectory as shown in Figure 3.3. Now we can see that the area enclosed between this curve and the x-axis is not convex. If we draw the line from the origin that is tangent to the plug flow trajectory (AB) we obviously make the convex hull of this region. If we now look at rate vectors on the straight line AB we find that there is a section over which they point outwards so that we do not as yet have the attainable region.

Now let us look at the point B. At this point the vector AB between the origin A and this point B is collinear with the rate vector at B (this is just the necessary and sufficient condition for AB being tangent to the plug flow trajectory). Thus point B satisfies the conditions for a C.S.T.R. with feed  $x = 1, y = 0$ . Thus the locus of C.S.T.R.'s will pass through point B. This locus might also be tangent to the rate vector at this point but this is extremely unlikely. Thus we would expect the locus to be either passing into the convex region or leaving it at this point. Either way this implies that except in the unlikely event of the double tangency condition, the C.S.T.R. locus will in part lie outside the convex hull of the plug flow trajectory. Let us now draw the C.S.T.R. locus, which does indeed pass through the plug flow trajectory at B.

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Figure 3.3: Van de Vusse Example with  $a_1 = 20$ ,  $a_2 = 2$

- — — — — C.S.T.R. from feed point A
- - - - - Plug Flow with feed point A
- - - - - Plug Flow with feed point C
- Tangent lines from feed point A to plug flows at B and C



The C.S.T.R. locus is itself not convex. Let us thus draw the straight line from the feed point that is tangent to the C.S.T.R. locus i.e. line AC. At point C there will be a plug flow trajectory which will start tangent to the C.S.T.R. locus as at point C we know the rate vector is collinear with AC. This plug flow trajectory starts above the previous plug flow trajectory and as we know they cannot cross, it must always stay above.

Let us look at the rate vector along the line AC. At point A its slope is obviously less than AC while at point C it is equal to AC. If it took on the value equal to AC between points A and C a part of the C.S.T.R. locus would cross the line AC. Thus because the rate vector is continuous we know that the rate vector does not point outwards along the whole of AC. This result will of course always be true for a straight line forming the convex hull of the C.S.T.R. locus in two dimensions.

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Let us now examine the region bounded by the line AC, the plug flow trajectory from C to (0,0) and the axis from (0,0) to (1,0). This is a convex region and if we look at the rate vectors on the boundary they all point inwards, are tangent or are zero. Again if we examine the complement of this region conditions (c) and (d) are true so that this region satisfies the necessary conditions for the attainable region. If our aim is again to maximize  $y$ , then based on this region we can achieve this by a C.S.T.R. from A to C followed by a plug flow until we have the rate vector horizontal giving a value of  $y = 0.071$ . The configuration of a C.S.T.R. followed by a plug flow was also found to be optimal by Chitra and Govind (1985a) for the case where  $a_1 > a_2$ .

### 3.2.2 Example 2: Trambouze Kinetics

We now look at the Trambouze example. The reaction is a parallel, irreversible decomposition of A to form B (zero order reaction with rate constant 0.025 mol/l min), C (first order reaction with rate constant 0.2 /min) and D (second order reaction with rate constant 0.4 l/mol min). We wish to optimize the selectivity of A to C. Previous work on this problem has been discussed in section 1.3.2. Using these kinetics and objective function we need only work in two dimensions; namely concentration of A and concentration of C. We normalize our variables such that:

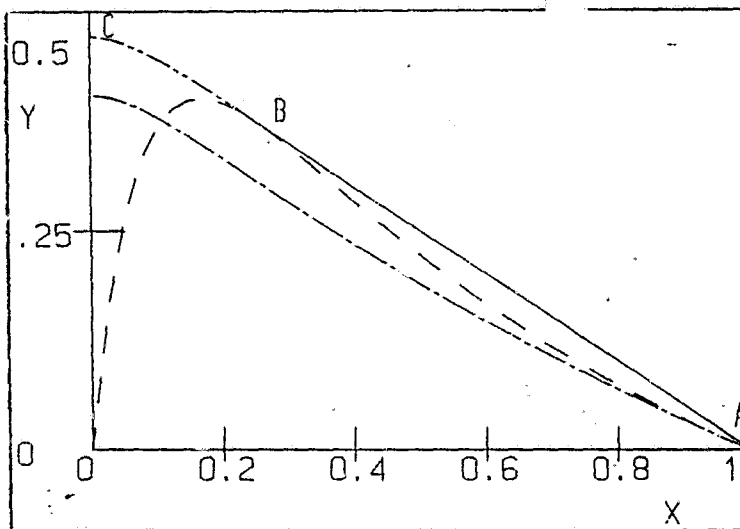
$$x = c_A / c_A^0 \quad \text{and} \quad y = c_C / c_A^0$$

where  $c_A^0$  is the concentration pure A and is taken as 1 mol/l. We draw the plug flow trajectory from the feed point  $x = 1$  and  $y = 0$  as shown in Figure 3.4. The curve, as can be seen from the figure, is not convex.

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Figure 3.4: Trambouze Example

- — — — — C.S.T.R. from feed point A
- - - - - Plug Flow with feed point A
- - - - - Plug Flow with feed point B
- Tangent line from feed point A to plug flow at B



Using the same reasoning as in the previous example, we draw the C.S.T.R. locus from the feed point. This locus is itself not convex so we draw the straight line from the origin that is tangent to the C.S.T.R. locus i.e. line AB. The rate vector points inwards along line AB and at point B is collinear to the line. The plug flow trajectory that starts from point B extends our region as shown in the figure. The region bounded by line AB, the plug flow trajectory from B (BC), the y-axis between the plug flow equilibrium (C) and (0,0) and the x-axis is convex. The rate vectors on the boundary either point inward, are tangential or are of zero magnitude. Conditions (c) and (d) are also met so this region satisfies the necessary conditions for the attainable region.

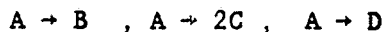
Suppose we now wish to maximize the selectivity defined as  $y/(1-x)$ . The objective function is a straight line which rotates around point A. The maximum selectivity would correspond to the line with the most negative slope that still

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lies in or on the boundary of the attainable region. Thus from the figure it is clear that we could rotate a line around A until it lay on AB. The points on AB are all solutions of our objective function and correspond to a selectivity of 0.5. These points could be achieved by a C.S.T.R. operating at point B with varying amounts of bypass. Paynter and Haskins (1970), in comparison, reported an optimal configuration of a C.S.T.R. in series with a plug flow reactor with selectivity of 0.5 while Achenie and Biegler (1986a) found an optimal configuration of two C.S.T.R.'s in series with selectivity of 0.4999. It would seem from these results that there was not only numerical error but shortcomings as well in the methods as the multiple solutions of the objective function were not found.

### 3.2.3 Example 3: Modified Non-Constant Density Trambouze Kinetics.

We again look at the Trambouze kinetics, but now modified to allow for the effect of density changes on the construction of the attainable region. The reaction is again a parallel irreversible decomposition of A to form B (zero order reaction with rate constant 0.025 mol/l min), C (first order reaction with rate constant 0.2 /min based on rate of reaction of A) and D (second order reaction with rate constant 0.4 l/mol min). The reaction rates are based on the following scheme:

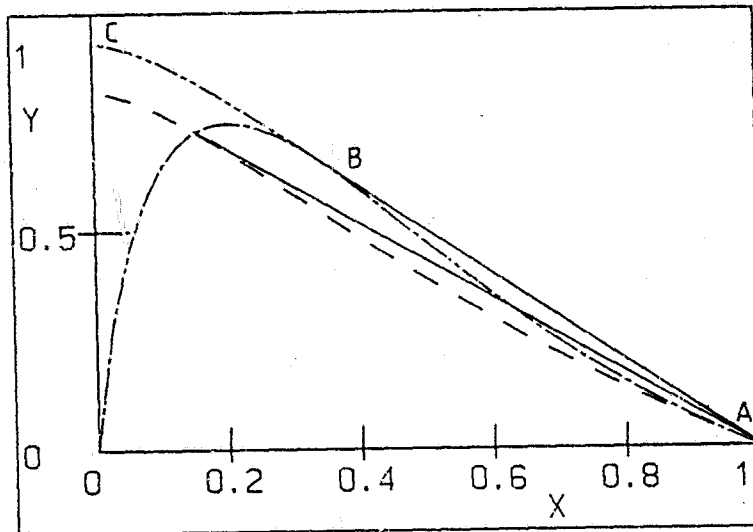


We have modified the reaction forming C so that the number of moles is no longer conserved. We will assume the reaction occurs at constant temperature and pressure in the gas phase and that the reaction mixture behaves ideally. We wish to optimize the selectivity of A to C. Using these kinetics and objective function we need only work in two dimensions namely  $d_A$  and  $d_C$ . We will normalize our variables such that  $x = d_A/d_A^\circ$  and  $y = d_C/(2d_A^\circ)$  where  $d_A^\circ$  refers to pure A and is taken as 1 mol/l. The construction of the attainable region is essentially the same as that of the constant density example of section 3.2.2, and is shown in Figure 3.5.

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Figure 3.5: Trambouze Example Modified for Non-Constant Density System.

— — — — — Plug Flow from feed point A  
 - - - - - C.S.T.R. with feed point A  
 - - - - - Plug Flow with feed point B  
 ———— Tangent lines



The region bounded by the straight line AB; the plug flow trajectory from B (BC); the y-axis between the plug flow equilibrium (C) and (0,0); and the x-axis satisfies the conditions for the attainable region.

If we define selectivity as  $d_C / (d_A^0 - d_A)$ , which by comparison is equal to  $2y / (1-x)$ , we find that we maximize selectivity along line AB and all points on this line could be achieved by a C.S.T.R. from the feed with bypass. The maximum selectivity in this case is 2.05.

3.2.4 Example 4: Modified Van de Vusse Kinetics.

We can now examine a more complicated example which has the same reaction network as the van de Vusse example, but has more involved kinetics.

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We can construct examples with possibly unrealistic kinetics but with a few concavities in the plug flow trajectory in the following way. Let as before  $y = c_B/c_A^\circ$  and  $x = c_A/c_A^\circ$ . Then for the plug flow trajectory let:

$$y = f(x) \left[ \ln \frac{x}{x_c} + \frac{y_0}{f(x_0)} \right] \quad (3.5)$$

Then it can be shown that:

$$\frac{dy}{dx} = \frac{f(x)}{x} + \frac{f'(x)}{f(x)} y \quad (3.6)$$

where  $f'(x)$  is the derivative of  $f(x)$  with respect to  $x$ .

Thus we have the ratio of the rates of formation given by:

$$\frac{r_y}{r_x} = \frac{f(x)^2 + xf'(x)y}{xf(x)} \quad (3.7)$$

Now by choosing

$$f(x) = 6x^6 - 6x^5 + 9x^4 - 16x^3 + 9x^2 - 2x \quad (3.8)$$

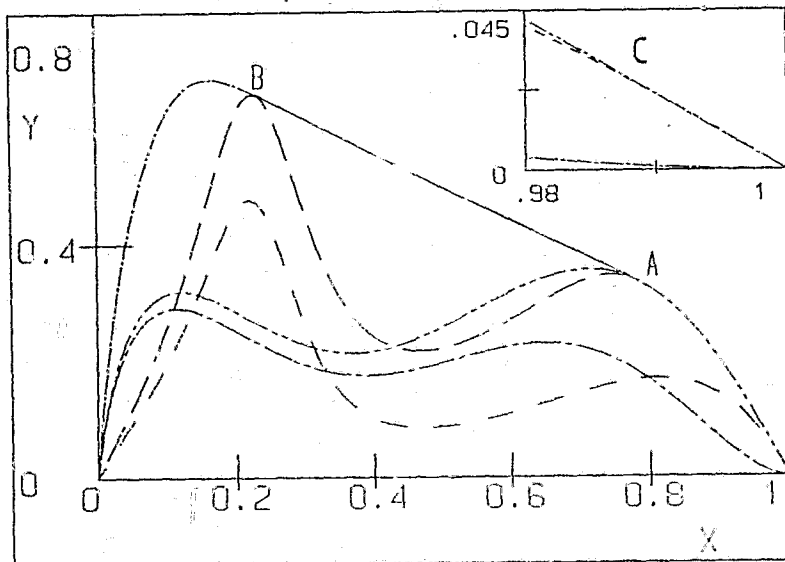
we obtain the plug flow curve shown in Figure 3.6. Note that we have presented the general solution in equation (3.5) as we wish to be able to draw plug flow trajectories starting with any feed. Note also that for equation (3.5) with:

$$f(x) = - \frac{x}{1 + a_1 x} \quad (3.9)$$

we have the plug flow equation for the van de Vusse kinetics with  $a_2 = 1$ .

Figure 3.6: Van de Vusse Reaction with Complicated Kinetics

- — — — — C.S.T.R. from feed point
- - - - - Plug Flow from feed point
- - - - - Plug Flow with feed point C
- — — — — C.S.T.R. from A
- . - . - . Plug Flow from feed point B
- — — — — Tangent line from plug flow A to C.S.T.R. at B



The plug flow trajectory starting from  $x = 1$  and  $y = 0$  has two concavities, one at the beginning and another in the middle. Let us again draw the C.S.T.R. locus from the origin which must pass through the point on the plug flow trajectory which is tangent to the straight line from the origin. The initial part of the diagram is enlarged and shown in the upper right hand corner of Figure 3.6. As before part of the C.S.T.R. now lies outside the convex hull of the plug flow trajectory but it is itself concave at the beginning. We draw the line from the origin which is tangent to the C.S.T.R. locus and from this point draw a new plug flow trajectory. This new plug flow trajectory still has a concavity in the middle and so we know that if we form the convex hull, the C.S.T.R. with feed at the tangent point with the lower value of  $x$ , will pass through the tangent point with the higher value of  $x$ . If we draw this C.S.T.R., we find it still has a concavity.



However what we really wish to find is the point A on the plug flow trajectory from which when a tangent is drawn to the C.S.T.R. locus at point B (with A regarded as the feed) is also tangent at A to the plug flow trajectory. From B we now draw the new plug flow trajectory and find that the region we have now drawn obeys our necessary conditions. Thus our maximum value of y we can obtain is 0.68 which is achieved by a C.S.T.R. followed by a plug flow followed by another C.S.T.R. followed by a final plug flow.

As before it is clear when we fill in the concavities on the C.S.T.R. loci with the appropriate straight lines that the reaction vectors cannot point outwards along these straight lines.

### 3.2.5 Example 5: Iso-Thermal Kinetics with Multiple Steady-States.

Let us look at an example where we can find a region which satisfies conditions (a) and (b) but not (c) and (d). We will use the same reaction network as before but with rates of formations given

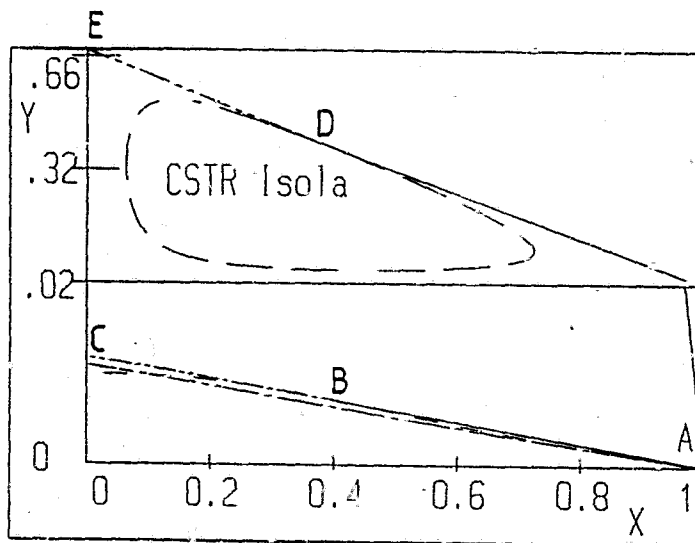
$$r_x = -k_1 \left[ x + \frac{bx^2y^2}{1 + Kxy^2} + ax \right] \quad (3.10)$$

$$r_y = k_1 \left[ x + \frac{bx^2y^2}{1 + Kxy^2} \right] \quad (3.11)$$

with given feed  $x = 1$ ;  $y = 0$  and  $a = 100$ ,  $b = 1000$  and  $K = 40$ .

Figure 3.7: Example with Multiple Solutions for the C.S.T.R.

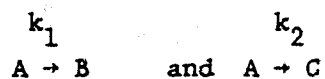
- — — — C.S.T.R. from feed point A
- - - - - Plug Flow from feed point A
- - - - - Plug Flow from tangent to C.S.T.R. locus
- Tangent line from feed A to C.S.T.R. locus



Now here the C.S.T.R. locus is given by two separate curves as shown in Figure 3.7 where in particular the one branch is an isola. It is possible using the techniques described in the previous examples to find the region given by ABC and the two axes which satisfies the first two of the necessary conditions for the attainable region but is not that region. Once we recognize the other branch of the C.S.T.R. curve we see that we can mix concentrations from our initial region with those in the isola to obtain the enlarged region ADE and the two axes which now satisfies the full necessary conditions. In this case we needed to establish for the initial region that there were no rate vectors outside the region which could be extrapolated back into the region. If this were indeed the case, then obviously no C.S.T.R. with feed in the initial region could take us outside the initial region.

## 3.2.6 Example 6: Adiabatic Example with Multiple Steady States

In Example 5 above, we considered a fairly artificial example where the C.S.T.R. locus had multiple branches. This type of situation arises fairly often in non-isothermal reactor systems even with simple kinetics. We now consider an adiabatic reactor system with the following kinetics:



$$r_A = -k_1 c_A^2 - k_2 c_A \quad (3.12)$$

$$\text{and } r_B = k_1 c_A^2 \quad (3.13)$$

where  $r_i$  is the rate of formation of species  $i$ ,  $c_i$  is the concentration of species  $i$  and  $k_1$  and  $k_2$  are rate constants. For this example we will construct the attainable region in concentration space which will allow us to determine all feasible concentrations of A and B.

We can write that:

$$\frac{r_B}{r_A} = \frac{-k_1 c_A}{k_1 c_A + k_2} = \frac{-(k_1/k_2) c_A}{(k_1/k_2) c_A + 1} = \frac{-a}{a+1} \quad (3.14)$$

We will refer to  $(c_A/c_A^0)$  as  $x$  and  $(c_B/c_A^0)$  as  $y$ . The plug flow equation can be written, with the temperature dependence included, as follows:

$$\frac{dy}{dx} = \frac{-a}{a+1} \quad (3.15)$$

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where

$$a = (k_1 c_A^0 / k_2) x = \exp(11.5 - 5000/T) x \quad (3.15b)$$

$$T = T_{in} + (540-100)y + 100(1-x) \quad (3.15c)$$

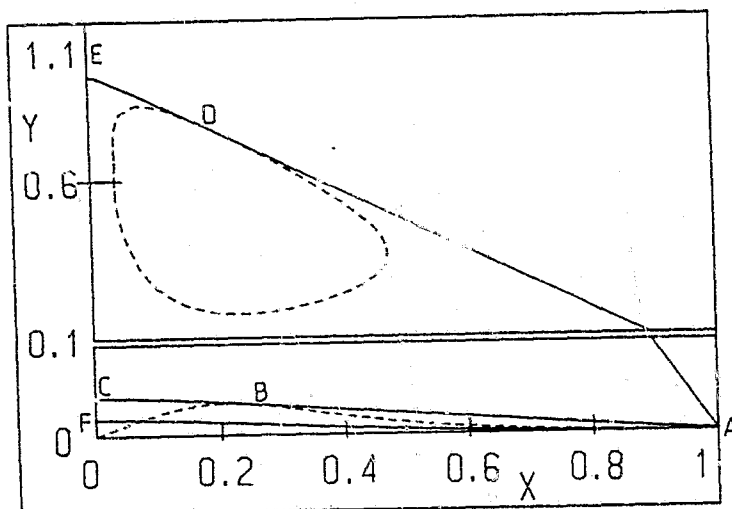
$$T_{in} = \text{inlet temperature, ie at } x=1 \text{ and } y=0. \quad (3.15d)$$

Equation (3.15c), is the constant pressure energy balance where  $\hat{C}_p$ , the specific heat of the mixture, and the enthalpy of reaction are constants.

The inlet concentration corresponds to  $x = 1$  and  $y = 0$  and we will use an inlet temperature of 290. If the attainable region is constructed in concentration-space in the manner discussed in the previous examples, we find that the plug flow trajectory AF

Figure 3.8: Adiabatic Example with Multiple Solutions for the C.S.T.R.

- — — C.S.T.R. from feed point A
- Curve AF: plug flow from feed A
- Curve BC: plug flow from feed B
- Curve DE: plug flow from Feed D
- Line AB: tangent line to C.S.T.R. at B
- Line AD: tangent line to C.S.T.R. at D



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from the feed concentration A lies close to the x-axis as can be seen in the bottom part of Figure 3.8. The C.S.T.R. locus from the feed point has three branches. If only the one branch is considered, one can find a region ABC which lies close to the x-axis, that satisfies parts (a) and (b) of the necessary conditions. One however finds that conditions (c) and (d) are not met.

The other two branches of the C.S.T.R. locus enlarge the attainable region quite considerably and form a region given by the x-axis, straight line AD, the plug flow trajectory from D (DE) and the y-axis from the origin to point E. It is found that the reaction vector points inwards along line AD and the x-axis and is zero along the y-axis. Necessary conditions (c) and (d) are also satisfied by this enlarged region.

It can be seen that the multiple branches of the C.S.T.R. arise even with simple kinetics for non-isothermal systems. These branches must be included in the attainable region and they may enlarge the attainable region quite considerably when compared with the region constructed using only one branch of the C.S.T.R. locus.

### 3.2.7 Two Dimensional Optimization in Concentration Space

The method by which we have satisfied the necessary conditions in these two dimensional examples is by the procedure of alternately drawing a plug flow trajectory, checking if the region it encloses is convex, and if not, drawing the C.S.T.R. which effectively bridges the gap caused by the concavity. We repeat this procedure starting from the origin and as each C.S.T.R. bridges a finite gap the process must terminate in a finite number of stages.

We then check that conditions (c) and (d) are satisfied and if they are not we extend the region appropriately. It has been shown that a recycle reactor need never be considered as part of the boundary and therefore it is clear from our construction

that for a two dimensional system, except for the base, the boundary of the attainable region must be achieved by a sequential process and must consist of alternate straight lines and plug flow trajectories. The straight lines are of course the bridges built by the C.S.T.R.'s. Thus we may achieve any point on the boundary, excluding the base, either by a series of C.S.T.R.'s or plug flow's with a possibility of some bypass of the last reactor if it is a C.S.T.R. (This will enable one to attain intermediate points along the straight line).

Now in order to perform the optimization we must have an objective function which depends only on  $x$  and  $y$ . If the curves of constant objective function plotted in the  $x$ - $y$  plane have no closed contours in the attainable region then the optimum must lie on the boundary of the domain and we can calculate its best value and the associated values of  $x$  and  $y$  by drawing the appropriate contours. For the case of maximizing  $y$  the contours are horizontal straight lines.

If the objective function has closed contours in the domain then we must check the optimum point in the domain relative to the best boundary point. If the optimum does lie on the interior of the domain there will be infinitely many ways of achieving it but because of the convexity of the domain one can always achieve it by mixing between boundary points which is equivalent to a series-parallel arrangement of reactors.

### 3.3 Examples in Concentration-Time Space

#### 3.3.1 Example 7: The Unconstrained and Constrained Attainable Region for Adiabatic Reaction.

In this example, for a single constant density reaction system and an adiabatic system of reactors, we examine the following three cases:

- (a) construct the attainable region in concentration-time space.

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(b) find the attainable region when using only plug flow reactors.

(c) find the attainable region when using only C.S.T.R.'s.

In the last two cases we have specified the type of reactor to be used. These problems will be referred to as constrained attainable regions (see section 2.4.1).

We will define the rate of formation as:

$$-r = 5E5 \exp(-4000/T) c - 5E8 \exp(-8000/T) * (1-c) \quad (3.16)$$

where  $c$  is concentration. The temperature for an adiabatic constant pressure process with constant specific heat and heat of reaction is given by:

$$T = T_b^0 + T_{ad}(1-c) \quad (3.17)$$

We will use a feed concentration of 1, temperature  $T_b^0$  of 300 and  $T_{ad}$  of 300. We define  $T_b^0$  as the basis temperature of a stream, i.e. the temperature of any stream when it consists of pure feed material or alternatively when  $c = 1$ . Thus, for this case, the basis temperature is  $T_b^0$ .

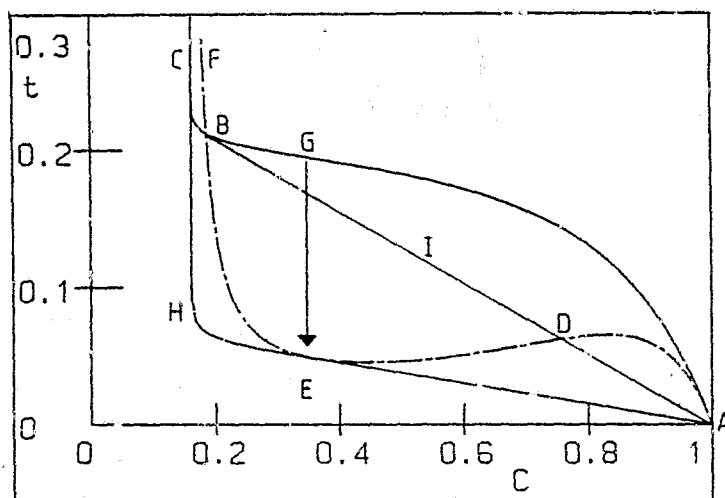
### Construction of the attainable region

Starting at the feed concentration of 1 and a time of 0 we can draw the plug flow trajectory AGBC on the concentration-time axes. This trajectory is a concave curve for part of its trajectory as shown in Figure 3.9. We are not able to draw the plug flow reactor all the way to the equilibrium point but have stopped at some arbitrary, large time. We fill in the concavity of the plug flow trajectory by mixing feed (given as point A on Figure 3.9) and material at concentration B where the straight line AB is tangent to the curve AGBC at point B.

The reaction vector is in this case  $(r, 1)$  and is a function of concentration only. The slope of the plug flow trajectory is equal to that of the reaction vector and, as drawn in Figure 3.9,

Figure 3.9: Attainable Region for Adiabatic System with no Constraints

- - - - - C.S.T.R. from feed point A  
 Curve AGBC: Plug Flow from feed A  
 Curve EHC: Plug Flow from feed E  
 Line AB: tangent to plug flow AGBC  
 Line AE: tangent to C.S.T.R.



is simply the inverse of the rate of formation of C or in other words  $(1/r)$ . We can therefore see directly from the plug flow trajectory AGBC by a simple downwards translation of the curve (because it is a function of C only) how the reaction vector varies along line AB. It can be seen that there is a section of the line over which the reaction vector points outwards. We therefore have not yet found the lower boundary of the attainable region.

- At points B and D the slope of the reaction vector is equal to that of line AB and these points are therefore solutions to the equation of the C.S.T.R. with feed A. If we draw in the C.S.T.R. locus ADEF from point A, it passes through points B and D and lies beneath line AB between B and D. The C.S.T.R. locus is itself not convex. We can draw a straight line between points A and E which fills in the concavity and represents mixing between these two points.



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- From the slope of the plug flow trajectory we can see that the reaction vector points inwards along line AE and is collinear at point E. Along the boundary EF formed by the C.S.T.R locus the reaction vectors point outwards. We therefore draw in the plug flow trajectory EHC from point E. As the reaction vector is a function of concentration only, the slope of the plug flow trajectory is the same for all times at the same concentration, and thus the trajectory of the second plug flow is the same as that of the first plug flow but shifted downwards so that point G corresponds to point E.

The lower boundary of the region is now given by AEHC. (Note that in the limit the concentration tends to zero and  $t \rightarrow \infty$ ). The other boundary line is the vertical from A, formed by mixing feed with the equilibrium material. No reaction vectors point outwards along this boundary and the boundary is convex. No reaction vectors in the region below this boundary, when extended backwards, intersect the boundary. A plug flow trajectory in the region below this boundary can also not be intersected twice by a line from the boundary. We thus have satisfied our necessary conditions for the attainable region.

If we wish, for instance, to find the minimum residence time for a given outlet concentration, the answer would lie on curve AEHC. Any point above this boundary can be reached as well. For example, if we wished to operate our system at point I, we could use a plug flow reactor operating at point B with bypass so as to give us an outlet condition corresponding to point I. It is interesting to see how in this case the residence time of the system with this outlet concentration is less than that of the plug flow reactor alone.

### (b) Attainable Region using only Plug Flow Reactors.

We accept that bypassing is a plug flow reactor of zero space time in parallel with another reactor.

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We will now use only plug flow reactors and we will look at constructing the attainable region. We can use this attainable region to find the reactor configuration to minimize the total residence time for a given output concentration.

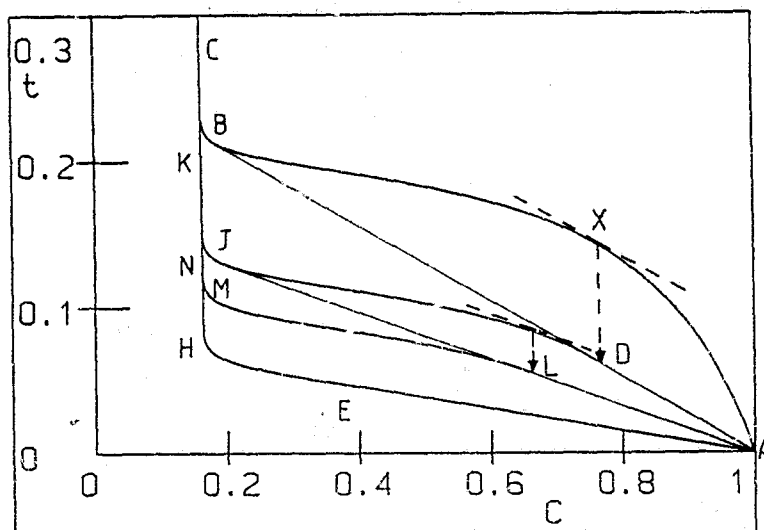
- The plug flow trajectory from the feed point is given in Figure 3.10 by curve AXBC and corresponds to curve AGBC in Figure 3.9. Notice that the time refers to the residence time of the system, which in this case is a plug flow reactor. By allowing bypassing and mixing from any point along the plug flow trajectory with any other point along the trajectory we obtain the attainable region for a single plug flow trajectory with bypass, the boundary of which is given by ADBC and a vertical line from A. Line AB of the boundary fills in the concavity of the plug flow trajectory and BC is part of the plug flow trajectory. The time still refers to the residence time of the system, which can now consist of a plug flow reactor with some bypass. For example, we can mix fluid from the plug flow reactor with residence time B with feed material given by point A in such a ratio so as to produce material of concentration and residence time represented by point D.

- We now wish to choose the second plug flow reactor such that the boundary of the attainable region is lowered as much as possible.

There are two points to consider when choosing the second reactor. Firstly the plug flow trajectory for an adiabatic reactor is of fixed shape as the initial conditions are unique (see Result 5, Section 2.6.1). Thus the plug flow trajectory from feed point D, for example, is just the original trajectory AXBC shifted down until point X on curve AXBC touches point D. We will refer to the trajectory AXBC as the base trajectory. Furthermore, as temperature depends only on concentration in this adiabatic system, the temperature at point D must be the same as point X. Thus when shifting the base trajectory as described we always automatically fulfil the adiabatic relationship. Consequently, as the plug flow trajectories cannot cross each other and there is only one base trajectory, the required second trajectory must be the one that when moved downwards is the lowest for all possible feeds to the second reactor or alternatively extends the region the most.

Figure 3.10: Attainable Region for Adiabatic System using only Plug Flow Reactors

Curve AXBC: Plug Flow from Feed A  
 Curve DJKC: Plug Flow from Feed D  
 Curve LMNC: Plug Flow from Feed L  
 Curve EHC: Plug Flow from Feed E  
 Line AB: tangent to plug flow AXBC  
 Line AJ: tangent to plug flow DJKC  
 — — — tangents to plug flow trajectories



If we do this we find the best feed point is point D on line AB where the slope of AB equals that of the plug flow trajectory (and therefore the slope of the reaction vector or simply  $(1/r)$  ).

This result occurs because the plug flow trajectory cannot move out of the one reactor attainable region between A and D as the reaction vectors point inwards along AD. Point D is the first point at which the plug flow trajectory may move outside the attainable region as the gradient of the reaction vector is equal to the slope of line AB. This trajectory must also be the lowest as plug flow trajectories cannot cross and consequently trajectories with feeds between DB must lie higher than the one from D. The trajectory of the second plug flow reactor is given by curve DJKC.

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We can again mix every point that can be reached by the system of reactors with every other point and so obtain the two reactor attainable region, the boundary of which is given by ALJKC and a vertical line from A. The boundary ALJKC represents the relationship between the minimum residence time for all possible outlet concentrations for a two stage adiabatic plug flow reactor system.

- The same considerations that held for the second plug flow reactor would again hold when choosing the third stage. We would thereby find the feed to the third stage to be point L where the slope of line AJ would again be equal to that of the (base) plug flow trajectory. The third plug flow reactor would operate along curve LMNC and the boundary of the attainable region for a three stage reactor system would be given by line AM and the plug flow trajectory MNK.

It is interesting to see that the change in the boundary of the attainable region between two and three stages is much smaller than that between one and two stages and how the tangency point moves towards the left. Each additional stage would give a smaller and smaller change in the boundary of this limited attainable region until, in the limit, we would reach the lower boundary of the whole attainable region - AEHC. At point E, the slope of the base plug flow trajectory, and consequently line AE, is a minimum. Curve EHC is the trajectory of the plug flow reactor with a feed point at E. It would take an infinite number of plug flow reactor stages to reach point E. The boundary AEHC of this attainable region fulfils all the necessary conditions and is therefore the attainable region that one could reach using any possible reaction and mixing processes and must correspond to the boundary found in the previous example. Point E by definition fulfils the equation describing the operation of a C.S.T.R and this is the same result as found in the previous example.

Notice how the concept of finding the reactor that will extend the attainable region the most is equivalent to the standard analytical optimization of finding the reactor that minimizes the residence time. By using geometrical arguments, we have found the

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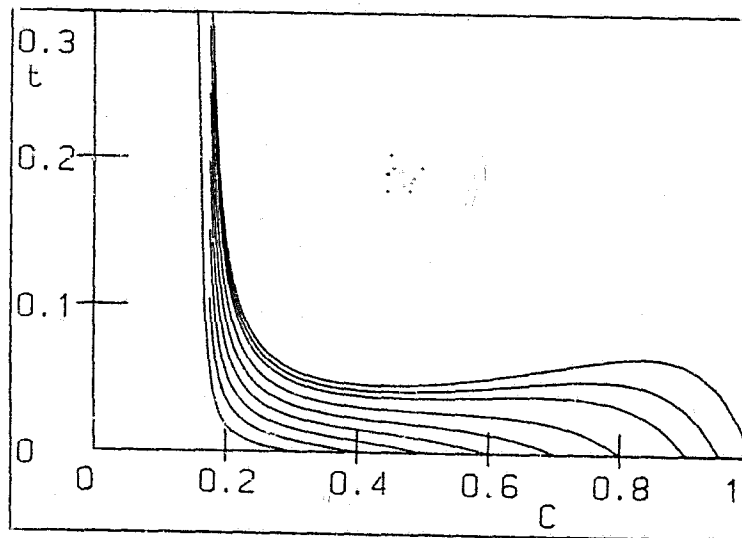
optimal adiabatic plug flow reactor system and in particular its structure. The reasons for the analytical conditions can also be clearly visualized.

(c) Construction of the Attainable Region using only C.S.T.R.'s.

We accept that bypassing is a C.S.T.R. of zero space time in parallel with another reactor.

We will now only use C.S.T.R.'s and we will look at optimizing the reactor configuration to minimize residence time. The construction for C.S.T.R.'s is different from that of plug flow reactors as there is no longer a unique, base locus although the reaction vector is still a function of concentration only. The shape of the locus will depend on the feed concentration only and a family of C.S.T.R. loci is given in Figure 3.11. All the loci obey the adiabatic relationship and so each feed-point has a related feed temperature which will vary depending only on the feed concentration.

Figure 3.11: Family of Iso-Enthalpic C.S.T.R. Loci from Various Feed Concentrations.

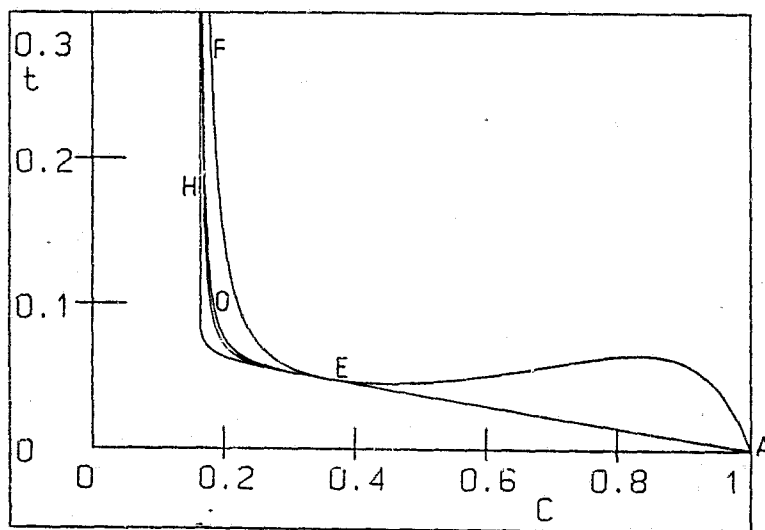


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In order to construct the one reactor attainable region we draw the C.S.T.R. locus for feed point A, giving curve AEF in Figure 3.12. We can form the one reactor attainable region for one C.S.T.R. by mixing every point on the locus with every other point. The lower boundary of the one reactor attainable region is given by the line AE which fills in the concavity on the C.S.T.R. locus and the section EF of the C.S.T.R. locus. In order to determine the best second reactor, we again draw the C.S.T.R. locus from every feed point and find the lowest curve. The C.S.T.R. loci along the boundary of the attainable region must lie lower than the equivalent curve starting from the higher residence times. The lowest curve must therefore originate from feed points on the boundary of the one reactor attainable region. All the reaction vectors along AE point into the one reactor attainable region. Any C.S.T.R. locus from these points must then move into the attainable region in order to satisfy the operating equation of the C.S.T.R. Point E satisfies the operating equation of all C.S.T.R. loci with feed points along AE and all the loci must pass through point E tangentially as the

Figure 3.12: Attainable Region for Adiabatic System using only C.S.T.R.'s.

- Curve AEF: C.S.T.R. from feed A
- Curve ED: C.S.T.R. from feed E
- Curve EH: limit to infinite number of C.S.T.R.'s in series
- Line AE: tangent to C.S.T.R. with feed A



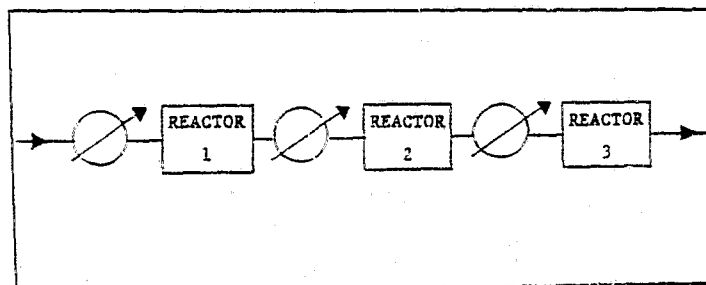
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slope of the reaction vector is a minimum at at this point. Thus no C.S.T.R. locus can take us below line AE. From point E the loci must lie further down than curve EF in order to satisfy the relationship between the slope of the reaction vector and the line joining the feed and locus points. From the geometry of the situation one can see that the C.S.T.R. locus from feed point E will have the lowest possible residence time for all the second stages. The lower boundary of the two reactor attainable region is AEO. We can repeat the construction for the third stage and we will find that the best reactor is the one with feed point just past E and this stage will extend the boundary of the two reactor attainable region a little way along curve EH. It will require an infinite number of C.S.T.R. reactors in series to produce the whole of the attainable region (line AE and curve EH) which is again a plug flow trajectory with feed E, or equivalently, an infinite number of C.S.T.R.'s in series.

### 3.3.2 Example 8: Interstage Cooling

We will now look at the problem of finding the attainable region for an interstage cooling reactor system as shown in Figure 3.13. In this reactor system we are allowed to heat the feed up to any temperature and follow this by a specified number of plug flow reactors in series with heat exchangers between each stage.

Figure 3.13: Non-adiabatic Example: Interstage Cooling Reactor.



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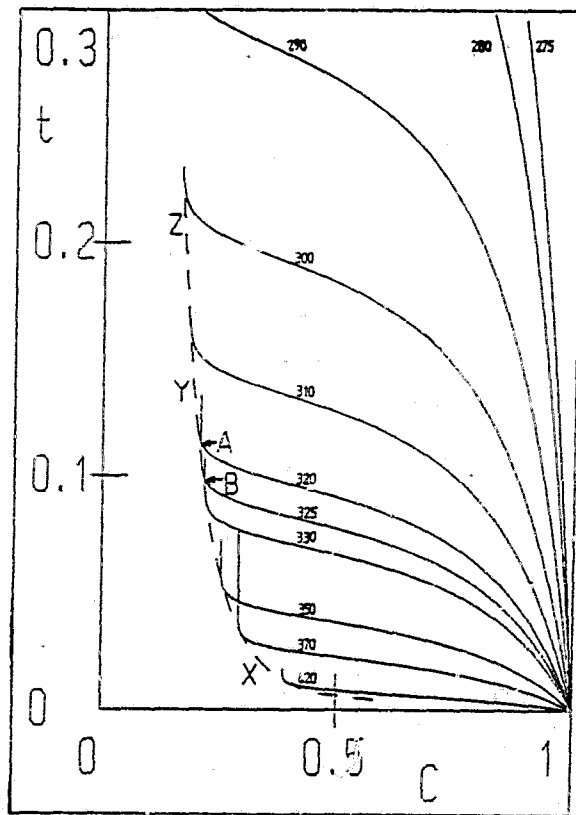
These effectively allow us to adjust the feed temperature to each stage. The reactor stages are all adiabatic in this situation but now each reactor stage can have a different basis temperature.

We will use the same rate expression and adiabatic relation as in Example 7. The previous work that has been done on optimizing this reactor is discussed in section 1.5.

Figure 3.14: Family of Adiabatic Plug Flow Reactors

———— Plug Flow trajectories for different basis temperatures  
- - - - Curve XYZ: boundary of the attainable region for a one stage adiabatic plug flow reactor system

*Basis temperatures are written on the plug flow curves.*





- The adiabatic plug flow trajectories for different basis temperatures (ie different values of  $T_b^0$  of equation (3.17)) are shown in Figure 3.14. Notice that the slope of these curves is equal to the slope of the reaction vector. We can find the convex hull of the trajectories and the boundary of the hull is given by the dotted line XYZ and a vertical line from (1,0).

- We will first consider the question of the best inlet temperature for a single stage reactor system. If we examine the plug flow trajectories with basis temperatures of 320, 325 and 330, we can see that the plug flow trajectory with basis temperature of 325 lies in the boundary for exit conditions between A and B. For concentrations lower than A, the plug flow trajectory with a basis temperature of 320 has a lower residence time than the plug flow trajectory with a basis temperature of 325. Similarly for concentrations higher than B, the plug flow trajectory with a basis temperature of 330 has a lower residence time than the plug flow trajectory of basis temperature 325. Thus, in the limit, the portion of a plug flow trajectory (of given feed temperature) that lies in the boundary is the point where the neighbouring curve, that is the curve with a infinitely small increase in the basis temperature but the same feed concentration, intersects it, ie:

$$\frac{\partial \tau}{\partial T_b^0} = \frac{\partial}{\partial T_b^0} \left( \int_{C^0}^{C^{ex}} \frac{1}{R} dC \right) = - \int_{C^0}^{C^{ex}} \frac{1}{R^2} \frac{\partial R}{\partial T} dC = 0 \quad (3.18)$$

This equation is general and gives the outlet concentration  $C^{ex}$  that a reactor of specified basis temperature should operate at in order to lie in the boundary of the attainable region, or in other words, describes the minimum residence time versus concentration relationship. When the specific heats are constant and the temperature-concentration relationship simplifies to equation (3.17),  $(\partial T / \partial T_b^0)$  is unity. Furthermore, if the density of the system is constant as well, equation (3.18) agrees with the results obtained by conventional optimization techniques (Horn, 1961 and Konoki, 1957). For one reactor systems, the attainable region boundary is given by the envelope of the extrema of the plug flow curves with different initial temperatures, that is the dotted line XYZ of Figure 3.14.

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- Let us now consider the best basis temperature for the next stage. We know that the outlet concentration of the first stage, which is also the inlet concentration to the second stage, must lie on the envelope shown in Figure 3.14. We must find the inlet temperature (or equivalently find the basis temperature) to the second stage reactor such that the trajectory of the reactor will extend the boundary of the attainable region as much as possible.

The condition to determine the boundary is more easily seen if we view the problem in a different way. We will rather specify the final basis temperature, and therefore the related plug flow reactor trajectory, that fulfils the adiabatic condition for the second stage. As an example, we specify the second plug flow trajectory given by curve ABC on Figure 3.15. The envelope of the attainable region from the first stage is shown as envelope XYZ. We must find the feed concentration to the plug flow trajectory ABC that will extend the attainable region the most. This is equivalent to finding the feed point that will move the trajectory of the second stage reactor as low as possible.

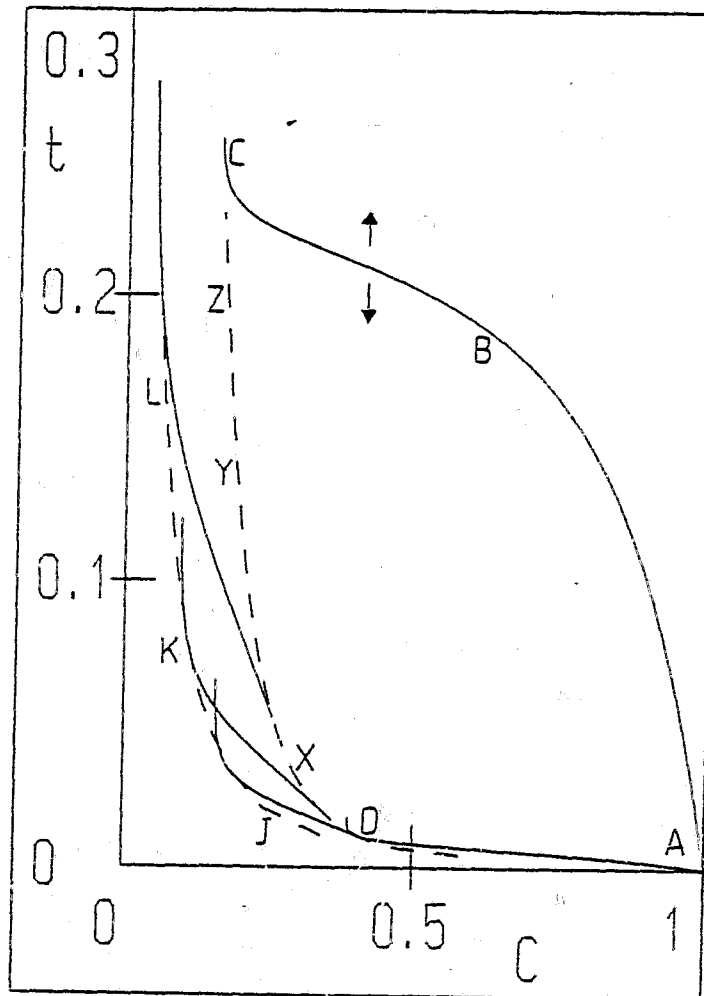
We do this by moving curve ABC up and down along envelope XYZ and in this manner find that this is the point on the envelope where the slope of the envelope (and therefore the slope of the plug flow trajectory that makes up that part of the envelope) equals that of the specified plug flow trajectory. Hence, this point occurs where the reaction vector at the outlet of the first plug flow stage equals that at the inlet to the second plug flow stage as at point D for trajectory ABC. This result must again hold for all reactor stages and agrees with the conventional mathematical optimization results (Horn, 1961 and Konoki, 1957).

We can repeat the process for all possible basis temperatures and again find the envelope formed by the intersection of neighbouring curves shown by envelope JKL. Envelope JKL represents the boundary of the attainable region for a two stage intercooled reactor system. It also represents the minimum residence time versus outlet concentration for all two stage interstage cooled reactors of the type shown in Figure 3.13. We

have again used geometric arguments for determining the attainable region and used this to perform the optimization. Again the reasons behind the optimization relationships can be clearly visualized. This construction can be repeated for three and greater number of stages and the optimal performance curves found for that number of stages.

Figure 3.15: Example of Interstage Cooling Reactor

- Curve XYZ: — — — Boundary of the attainable region for a one stage adiabatic plug flow reactor system
- Curve JKL: — — — Boundary of the attainable region for a two stage adiabatic plug flow reactor system
- Curve ABC: Second stage plug flow trajectory
- Curve AD: Best first stage reactor for second stage reactor ABC



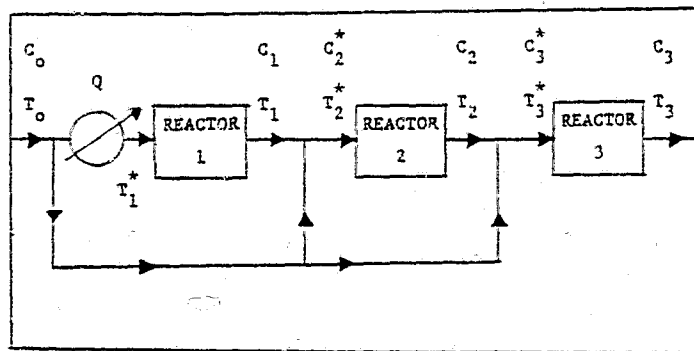
## 3.3.3 Example 9: Cold Shot Cooling

We will now look at finding the attainable region using cold shot cooling alone and hence the optimal reactor configuration to minimize the residence time for a given exit concentration using cold shot cooling. In this system we may heat up the feed to the the first plug flow reactor stage and add feed at its basis temperature between subsequent reactor stages as shown in Figure 3.16. We can thus vary the feed temperature to the first reactor, the residence time of the various reactor stages as well as the amount of bypass at each stage. We will use the same rate expression as in Example 7 and the same adiabatic relation although the method we use will hold for cases where the relation is more complex.

Previous work on this problem is discussed in section 1.3. The plug flow reactor trajectories for different enthalpies (ie different basis temperatures) are given in Figure 3.14.

The first stage of the construction will be identical to that of the previous example and as explained above, the dotted line XYZ of Figure 3.14 is the boundary of the attainable region.

Figure 3.16: Non-Adiabatic Example - Cold Shot Cooling Reactor.



- In order to find the boundary of the attainable region for the second reactor stage we will again consider the problem of which is the best feed point for a second plug flow reactor with specified basis temperature. The problem and construction is now different from the previous two examples as the whole process is not truly adiabatic. This is so because we have heated up the feed to the first reactor and thus different amounts of bypass give us different energy balance equations and hence different basis temperatures.

We will consider, for example, a second reactor stage with constant enthalpy such that the outlet stream has a basis temperature of 300 K. For each first reactor stage shown in Figure 3.14 we mix all possible outlet concentrations with the bypass (unheated feed which is assumed to be at 250 K in this example) in just the correct proportions to give the iso-enthalpic lines corresponding to a basis temperature of 300 K. These iso-enthalpic lines represent possible feed points for the second reactor stage and are shown in Figure 3.17 as curves DEF, GHI and JKL. For the simple iso-enthalpic relation used in this example, equation (3.17), the feed lines are simply a constant ratio of the length of the line between the outlet point and the feed point A. For each feed line we can move the plug flow trajectory ABC, which has a basis temperature of 300K, up and down until we find the feed point which gives the lowest possible second trajectory, or in other words, the trajectory that extends the attainable region the most.

This feed point is always the point where the plug flow trajectory ABC is tangent to the feed locus and it can be shown that it must therefore also be tangent to the first plug flow trajectory. This condition implies that the reaction vector at the outlet of the first plug flow reactor must be equal to that at the inlet of the second plug flow reactor which agrees with the mathematically obtained result (Konoki, 1960; Malengé and Vincent, 1972). We still however have not completed the construction. The best first stage for the given second reactor trajectory must still be chosen. We must therefore look at which first reactor stage gives the lowest second trajectory (as these translated trajectories ABC cannot cross each other) and this will be the best feed reactor for the given trajectory. In this

Figure 3.17: Example of Cold Shot Cooling Reactor

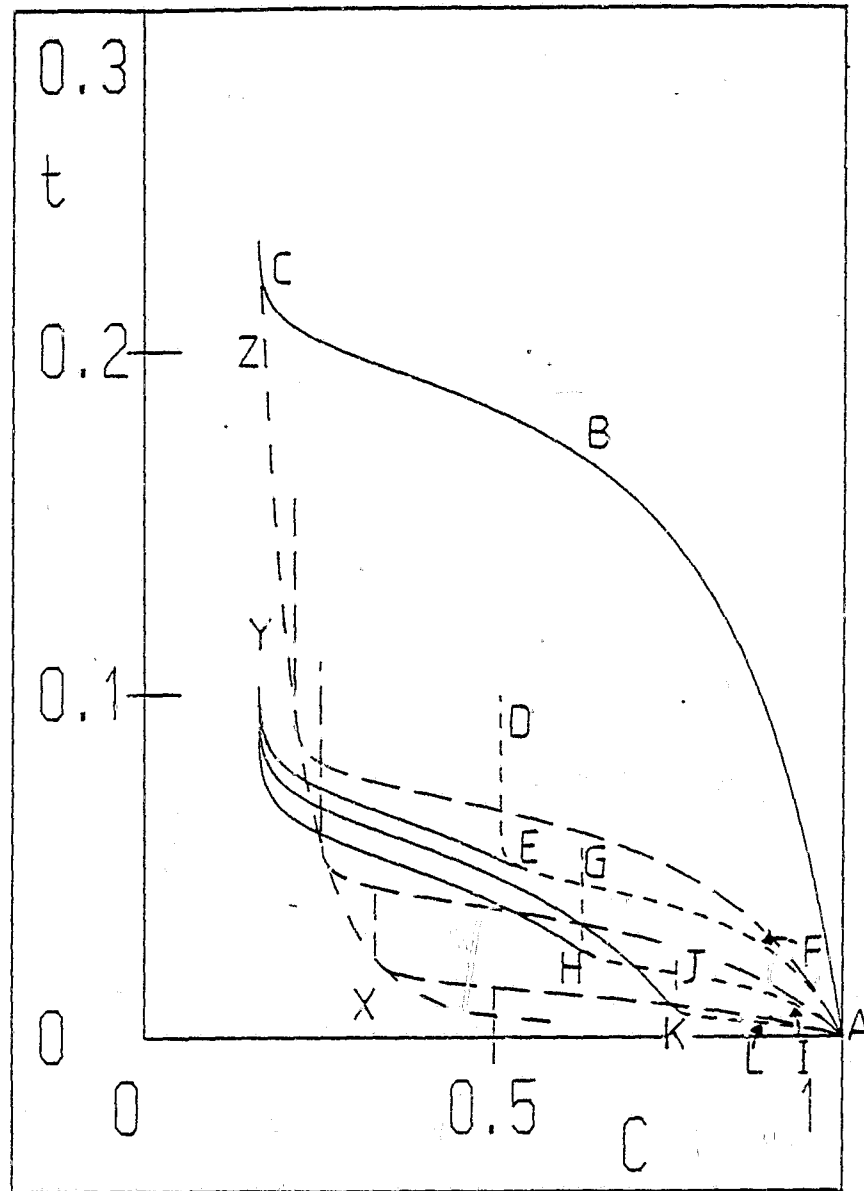
Curve XYZ: - - - - locus of optimal operating points for a one stage adiabatic reactor system

Curve ABC: ————— second stage plug flow trajectory

Curves DEF, GHI, JKL: - - - - iso-enthalpic feed lines

— — — — trajectories of the first stage plug flow reactors

————— lowest second stage plug flow trajectories from the iso-enthalpic feed lines



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case the feed locus GHI gave the lowest second stage plug flow reactor and thus the related plug flow trajectory must be the optimal first stage reactor. This can be done for all possible second reactor base temperatures and we will again find the envelope of the attainable region and hence the optimal operating points for a two stage reactor system.

We can repeat this construction for as many stages as required. The construction is fairly simple and only requires that one integrate each plug flow trajectory once. The calculation for the iso-enthalpic feed lines is especially easy in this example, but the construction method will hold for more complex energy balance expressions as well.

### 3.4 General Results in Two Dimensional Space

One needs to discuss in particular the results that foreshadow those that will be found in higher dimensions. These results arise from the answers to the following questions:

- (a) when will the plug flow reactor be best?
- (b) what can be said about the boundary of the attainable region?
- (c) why have only plug flow reactors and C.S.T.R.'s been found to define the boundary of the attainable region?

It is interesting that the attainable region can be constructed by using only plug flow reactors or only C.S.T.R.'s, as can be seen from the construction of the constrained attainable region in example 7, but an infinite number of construction steps are needed to construct the full boundary. By using both C.S.T.R.'s and plug flow reactors, the boundary of the attainable region can be constructed in a finite number of steps.

The answers to each of the following questions will be discussed separately below.

3.4.1 When will the Plug Flow Reactor be best?

The obvious answer to this is: when the trajectory is either only convex or only concave; ie if the second derivative of the variable of the y-axis with respect to the variable of the x-axis is all of the same sign along the plug flow trajectory. This is an easy way of thinking in two dimensions but does not help us to gain a feeling of what the answer will be in higher dimensions when the property of concavity or convexity cannot be so simply defined.

It is more helpful to think in the following way. Consider how the convex hull of the trajectory is made up. The property that we actually are interested in is whether all the points on the plug flow trajectory are convexly independent or not. We consider what this property means locally. If we are constructing the hull at some point along the trajectory, we find that we must join the point to each of its neighbouring points (by a straight line). If these two lines coincide ie have the same slope, this means that the point is not convexly independent with respect to its two neighbouring points. Thus the plug flow trajectory may not be convex. The reaction vector is, in the limit, equal to the slope of the line joining two neighbouring points on the plug flow trajectory. Thus in terms of the reaction vector, at the point on the trajectory where the convex independence breaks down, the derivative of the slope of the reaction vector with respect to the variable of the x-axis must be zero.

RESULT 21

Thus in higher dimensions the property of 'convexity' will also be related to the idea that the points on a convex hull must be convexly independent. The property of the second derivative being equal to zero is only applicable in two dimensional space.



3.4.2 The Properties of the Boundary of the Attainable Region?

The boundary of the attainable region will be made of sections with the following properties:

(i) neighbouring points where the reaction vectors are either tangential or point inwards on the boundary of this section of the region.

(ii) lines from a feed or equilibrium point  $C^*$  to another point  $C$  a finite distance away. The slope of the reaction vector at  $C$  must be the same as that of the line from  $C^*$  to  $C$ .

(iii) a line between endpoints, for example between a feed and an equilibrium point (ie the base of the attainable region), or between two feed points.

(iv) lines from a point  $C_1$  to a point  $C_2$ , where these points are not feed or equilibrium points. The slopes of the reaction vectors at  $C_1$  and  $C_2$  must be equal to that of the line joining  $C_1$  and  $C_2$ . One could extend this idea to any number of points that are collinear with the proviso that the slope of the reaction vectors must be equal to that of the line joining all the points.

RESULT 22

As we are assuming that we have a region where all the points are attainable, the provision that the slope of the reaction vector must be equal to that of the line follows as if it were not, a plug flow reactor could extend the boundary of the region. The straight line sections of the boundary would all have the reaction vectors pointing either inwards or tangentially, which would be fairly unusual from the properties of the C.S.T.R.

3.4.3 Why have only Plug Flow Reactors and C.S.T.R.'s been Found to Define the Boundary of the Attainable Region?

This question cannot yet be answered completely satisfactorily. However one might reason as follows. Consider the processes of reaction and mixing. Any local combination of reaction and mixing confines one to the plane defined by the reaction and mixing vectors (see Result 5). The resultant change in concentration must lie between the two vectors. However, in two dimensional examples, one is confined to a plane, and thus any differential process of mixing and reaction is worse in terms of extending the region than no mixing and only reaction, ie moving in the direction of the reaction vector only, or moving such that the mixing and reaction vectors are as far apart as possible ie the C.S.T.R. Thus in two dimensions, one could only expect that the boundary of the region would be constructed from plug flow reactors, C.S.T.R.'s and straight lines which fill in the concavities. Notice how the properties (ii) and (iii) of the previous section represent solutions to the C.S.T.R. equation and thus the extreme positions where the mixing and reaction vectors were 180 degrees apart.

Furthermore, one might conjecture from this discussion that condition (i) of the previous section should be modified to read that the reaction vectors would always be tangential, ie that the sections of the boundary of the attainable region where neighbouring points made up the boundary would always be sections of plug flow trajectories. One would not think that one could find a curved section of boundary made up from attainable, neighbouring points where all the reaction vectors pointed inwards.

Notice that in higher dimensions it would be possible to use reactors that involved differential mixing and reaction to construct the attainable region as these could move us in a different direction to the plug flow reactor or the C.S.T.R.

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One could postulate that by using only plug flow reactors, or only C.S.T.R.'s or both plug flow reactors and C.S.T.R.'s, one could construct the attainable region in any number of dimensions, but that an infinite number of stages may be required. By using reactors that allow simultaneous differential mixing and reaction, one could probably construct the region in a finite number of stages.

CHAPTER 4

THREE DIMENSIONAL EXAMPLES

4.1 Introduction

In this chapter, examples that can be done in three dimensional space will be discussed. These are examples where the reaction vector and the optimization functions depend on three or less independent variables. The structure of this chapter is different to that of Chapter 3. The implications of the property of convexity in three dimensional space and the consequences of this, which are not as obvious as the results in two dimensions, are firstly discussed. Furthermore, the properties of the convex hulls resulting from convex functions are discussed. When a geometrical structure is discussed in the theory, a reference to a specific example where this structure exists is given. It is suggested that if the reader has difficulty in visualizing the structures, the stereo figures of the example should be viewed to help with the interpretation of the theory.

The importance of Differential Reactors, that is reactors where differential mixing and reaction occurs, and their role in constructing the attainable region will be considered. After these points have been discussed, examples which illustrate the principles will be constructed.

One should note that the theory of convex sets of points is well developed. The results for discrete sets of points have been extrapolated and extended to continuous functions. The main difference is that the direction of the curve at a point is also

now important, ie in our case the reaction vector turns out to be important in constructing the hull. It was only while this thesis was being written up that a reference on convex functions appeared (Avriel 1988), but as the functions were not defined with respect to a vector field, it was not found to be directly applicable.

The viewing of three dimensional examples is obviously rather more difficult than in two dimensional examples. In order to show the geometry of the examples, stereo images have been used. These are discussed in Section 1.6.3. These stereo images are to be viewed through the viewer supplied in the back cover of the thesis. The attainable region is drawn in colour to show the axis and the reactors defining the boundary of the region. The construction steps are shown in some of the examples. The orientation of the axis is the same as in the completed attainable region so that the reader can orientate and understand the construction steps.

#### 4.2 The Property of Convexity in Three Dimensions

##### 4.2.1 Convex Functions

Consider some function that generates a curve in some three dimensional space. The set of points we will refer to as  $(C)$  and some individual point along the curve as  $C_i$ . The curve will have two end points ie the first and the last point on the curve, these we will refer to as  $C^o$ . What do we mean by a convex curve in three dimensions? If the set of points  $(C)$  is convexly independent, then all the  $C_i$  are extremal points and will be vertices of the convex hull of  $(C)$ . Similarly, we will define a Convex Function as one in which all the points of the function are extremal points and thus vertices of the convex hull of the function. For a set of points to be strictly convexly independent requires furthermore that at most three points lie in a plane. We will define a function in three dimensional space to be Strictly Convex if at most three points of the function lie

RESULT 23

in a plane. Similarly a function in n-dimensional space will be said to be strictly convex if a most n points of the function lie in an (n-1) dimensional hyperplane.

RESULT 24

#### 4.2.2 Structures Found in Convex Hulls in Three Dimensions

One would expect to find all the structures that were found in two dimensional convex hulls, ie

(i) neighbouring pairs of points (or, in other words, a part of the curve would lie in the hull); and

(ii) straight lines between points. The straight lines could join:

- an end point and a point along a curve.
- two end points.
- two points a finite distance apart on sections of a curve(s)

Furthermore, in three dimensions one could also expect to find:

(iii) planes between three points.

Theoretically and numerically, the boundary of a convex hull of a set of points in three dimensions is usually thought of as a set of planes. Notice that the intersection of two planes would be a line and that of two lines a point, in other words, a set of planes can give all the structures found in two dimensions. The structures found in two dimensions can give rise to curved surfaces and curved edges in three dimensional convex hulls.

The properties of these structures will be discussed in detail later. The properties of the surface of the convex hull of a plug flow trajectory will be discussed in Section 4.3.2 and the discussion will be generalized to the properties of the surface of the attainable region in Section 4.6.

#### 4.2.3 Types of Reactors that Could be Expected to Form the Boundary of the Attainable Region.

If we regard the reaction and mixing occurring in a reactor in terms of vectors, we have shown that the change in concentration is confined to lie in the acute angle between the mixing and reaction vectors (from Results 1 and 2). It follows that in general we could have the following processes forming the boundary of the attainable region:

(i) reaction only such that the change in concentration is in the direction of the reaction vector only (ie the plug flow trajectory).

(ii) reaction and mixing such that the vectors are collinear and pointing in opposite directions, ie in an extreme position. This is the C.S.T.R. locus.

(iii) The above two processes defined the boundary of the attainable region in two dimensions. In higher dimensions, however, it is possible that a combination of reaction and mixing, such as occurs in a differential reactors, could move us in a different direction to the above two processes and thereby extend the hull of the attainable region.

The properties of the optimal differential reactor and the situations in which this type of reactor is likely to extend the hull will be discussed later in Section 4.5.

#### 4.3 The Convex Hull of a Plug Flow Trajectory

The plug flow reactor is usually the first reactor that is used in constructing the attainable region. The properties of this curve are therefore very important and will be considered next. The discussion will later be extended to include other types of reactors and families of reactors.

#### 4.3.1 Visualizing the Process of Finding the Convex Hull of a Curve

The best way method to visualize the way in which the convex hull of a curve is formed, and the properties that are important in determining the shape of the hull, is as follows:

Take a piece of wire and form it in the shape of the curve one wishes to consider. Now take one of the end points and place this on a flat surface, such as a table. Move the wire until the neighbouring points lie in the plane of the surface. Thus the flat surface forms the face of the convex hull at that point. The flat surface is usually called the support plane. By rolling the wire so that the end point always touches the flat surface and that the other contact point moves along the wire, one can see how the surface of the hull is formed. When one cannot roll the wire any more then one starts with the other end of the wire and again rolls the wire to find the other side of the convex hull. This rolling procedure produces the other side of the convex hull. If one can roll the wire from one end point to the other, this means that the convex hull of this curve will be a type a fan structure, called a Fan Hull. This type of structure is illustrated in Section 4.7.2, Figure 4.6. If one cannot roll the wire from end point to the other, then at most a section of the face of the convex hull of the wire will be a fan hull. The rest of the face will typically be a plane or a surface formed by rolling the wire with two points on the curve touching the surface and eventually meeting at a point. These types of structures can be seen in Section 4.8.1, Figure 4.8c.

Note that 'rolling' the curve is equivalent to moving along the tangent of the curve, ie in the direction of the reaction vector. From considering the 'rolling' of a curve as described above, only the three types of structures described have been found. The properties of the curve that gives rise to each of the structures are discussed below:

(1) Fan structures. This type of structure exists as long as the curve lies all on the one side of the flat surface as one is



rolling the wire (equivalent to equation (4.1) derived further on in Section 4.3.3), and if the two end points can simultaneously touch the flat surface with the curve all on one side of the flat surface.

(ii) Planes. This type of structure exists when one may place the wire on the flat surface and at least three points touch the surface.

(iii) Curved surfaces formed by lines between two points on the curve where the reaction vectors at the points and the lines joining the points are coplanar. This type of structure arises when one can place the curve on a flat surface such that two points touch the surface and the curve lies all on one side of the surface.

#### 4.3.2 The Mathematical Interpretation of the Convex Hull of a Convex Plug Flow Trajectory

In the previous section, we considered the support plane (the table surface) fixed and moved the curve (the wire). The more usual mathematical approach, is to regard the curve as fixed and to move the support plane. This type of approach will now be used to deduce from a mathematical view the types of structures found in a convex hull of a convex plug flow trajectory.

Let the set of points that lie on the trajectory be denoted  $C$ , and let  $C_i$  be some point along the trajectory.  $C^o$  denotes an end point, i.e. the feed or equilibrium point, of the trajectory. As the trajectory is convex, all the  $C_i$  are extremal points, that is, all the points lie in the boundary of the convex hull and in fact are the vertices of the hull (see Result 23).

Consider a support plane at point  $C_i$ . A support plane is a plane containing  $C_i$  and positioned such that all the points in the hull, excluding  $C_i$ , lie on one side of the plane. Thus the plug flow trajectory does not pass through the support plane but is tangent to the plane. Thus the reaction vector at  $C_i$  must lie in the support plane.

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We now tilt the plane to find the extreme position(s) of the plane, i.e. the position in which it lies in the boundary of the convex hull of  $(C)$ . To form part of the boundary of the hull, at least one other point of  $(C)$  must lie in the plane and all the other points of  $(C)$  must lie in and/or on one side of the plane. We tilt the support plane, keeping  $C_i$  and the reaction vector in the plane, and consider each of the other points in  $(C)$  in turn. The only points that are candidates are either:

(i) the end points  $C^o$  or

(ii) another point in  $(C)$  where the reaction vector could also lie in the plane. That is the plane would contain two points and the two reaction vectors as well. This is a more unlikely occurrence than (i). (This could be extended more than two points, for example to  $m$ -points and  $m$ -reaction vectors or  $m$ -points,  $m$ -reaction vectors and an endpoint as well.)

The trajectory will not all lie on side of the support plane if a point that does not satisfy these conditions is used.

Now the neighbouring point of  $C_i$  also lies in the boundary convex hull. The extreme position of the support plane through it must also lie in the boundary of the hull and will also be defined by either an end point or a point and a reaction vector. The intersection of the two support planes i.e. that through  $C_i$  and the neighbour of  $C_i$ , will be a line.

The faces of the hull of a convex plug flow trajectory would thus contain:

- curved faces formed by lines from an end point to a point on the trajectory, i.e. the 'fan hull' described earlier. This is found to be the most common type of structure. It is found as a section of almost all hulls.

- curved faces formed by lines from one point on the trajectory to another point along the trajectory which is not an endpoint. The reaction vectors at each of the points and the line are all three coplanar. These structures, because of the constraints imposed by the reaction vectors, are rather uncommon.

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- planes where the structure changes from one type to another. These will in general be formed by an end point, two points and the two reaction vectors at the points; or two end points, a point and the reaction vector at the point; or three points and the three reaction vectors at the points.

One could include planes formed by n-points and n-reaction vectors or n-points and n-reaction vectors and an end point(s). However, these are not common by the nature of the kinetics and are special cases of the above.

Thus all the types of structures found by the 'wire rolling' technique have a mathematical interpretation. It is also clear that fan hull is the most commonly found type of structure as it requires less constraints on the the points lying in the support plane. It is interesting to note that all the these structures are found in convex functions, and the simple concavity of two dimensions is obviously rather more complicated in higher dimensions. The single, most obvious difference is that complex structures are found in the hull even of convex functions.

### 4.3.3 When will the Convex Hull of the Plug Flow Trajectory be a Fan Hull?

For the convex hull of a plug flow trajectory to be a fan hull, the trajectory must obviously be a convex function, ie all the points along the function must be extremal points. However, to exclude the possibility of the other types of complex structures being possible, the trajectory must have other properties as well. If we think in terms of the 'wire rolling' process, the rolling will stop because:

(i) the plane in which the curve lies at some point also contains an endpoint. Thus the curve would not be strictly convex. This would be a local break-down in the fan structure.

(ii) the endpoint and two other non-neighbouring points (and of course associated reaction vectors) lie in a plane. Again the curve would not be strictly convex, and this behaviour would imply a global break-down in the fan structure.

(iii) endpoint  $\underline{C}^\circ$ , the reaction vector at the endpoint  $\underline{R}(\underline{C}^\circ)$ , and some point along the curve  $\underline{C}$  and the reaction vector at that point  $\underline{R}(\underline{C})$  are coplanar. Again the curve is not strictly convex if this occurs, and there is again a global break-down in the fan structure.

RESULT 25

It is thought likely that it is necessary for the local break-down in the fan structure to occur before there is a global break-down. In other words, if the curve is everywhere strictly convexly independent locally with respect to endpoints, then it will be globally strictly convexly independent. This however has not been proved.

We will now derive the condition for a curve to be locally strictly convexly independent with respect to an end point.

Consider three neighbouring points along the trajectory:  $\underline{C}_{i-1}$ ,  $\underline{C}_i$ ,  $\underline{C}_{i+1}$ . The face of the hull at these points is made up by lines  $(\underline{C}^\circ, \underline{C}_{i-1})$ ,  $(\underline{C}^\circ, \underline{C}_i)$  and  $(\underline{C}^\circ, \underline{C}_{i+1})$ . If the fan structure is about to break-down, then  $\underline{C}_i$  must lie in the plane of  $\underline{C}^\circ$ ,  $\underline{C}_{i+1}$  and  $\underline{C}_{i-1}$ , ie the points are not strictly convexly independent. Thus, in the limit, the line  $(\underline{C}^\circ, \underline{C}_i)$  and the reaction vector at  $\underline{C}_i$ ,  $\underline{R}$  and the change in the derivative  $\underline{R}'$ , where  $\underline{R}'$  is equal to  $d\underline{R}/dr$ , must all be coplanar:

$$P = [(\underline{C} - \underline{C}^\circ) \times \underline{R}] \cdot \underline{R}' = 0 \quad (4.1)$$

The above is a necessary condition.

RESULT 26

As a sufficient condition one would need to prove that a global break-down in the fan structure could only occur when a local break-down occurred.

An alternative way of deriving equation (4.1) is as follows:

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The vectors  $\underline{R}$  and  $\underline{R}'$  are perpendicular to each other. The osculating plane is defined by these two vectors. A strictly convex curve will always lie on one side of this osculating plane. Thus:

$$\underline{b} = \text{binormal vector} = \underline{R} \times \underline{R}' \quad (4.1a)$$

The binormal is perpendicular to the osculating plane and for curve to lie on one side of the osculating plane:

$$P = \underline{b} \cdot (\underline{C}^o - \underline{C}) \text{ must be of one sign} \quad (4.1b)$$

Thus if at any point  $P = 0$ , then the curve will lie in the osculating plane and the curve and the endpoint will not be strictly convexly independent.

$$\begin{aligned} \text{ie } P = \underline{b} \cdot (\underline{C}^o - \underline{C}) &= (\underline{R} \times \underline{R}') \cdot (\underline{C}^o - \underline{C}) \\ &= [(\underline{C}^o - \underline{C}) \times \underline{R}] \cdot \underline{R}' = 0 \end{aligned} \quad (4.1c)$$

Thus equation (4.1) gives us, in principle, an easy check to see if the plug flow trajectory is locally strictly convex or not. In practice the algebra even for the simplest kinetics is generally very messy and it is easier to solve the equation numerically.

### 4.4 The Convex Hull of other Reactor Curves

All that has been said about the convex hull of plug flow trajectories will apply to any other reactor curve if instead of 'reaction vector' one substitutes 'tangent to the curve'. The tangent  $\underline{T}$  to the C.S.T.R. is, for example:

$$\frac{d\underline{C}}{dr} = \underline{T} = [ \underline{I} - r \underline{VR} ]^{-1} \underline{R} \quad (4.2)$$

where  $\underline{I}$  is the identity matrix, and  $\underline{VR}$  a matrix with element  $ij$  equal to  $(dR_i/dC_j)$ .

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Note that the method of visualizing the process of forming the convex hull of a curve as described in Section 4.3.1 will hold for any curve. The 'rolling' will be in the direction of the tangent to the curve, and thus the properties of the surface of the convex hull of a curve can be reformulated in terms of the tangent rather than the reaction vector.

### 4.4.1 The Check for a Fan Hull for any Reactor Curve

Again it is postulated that the convex hull of any arbitrary reactor curve, with end points  $\underline{C}^0$  and tangent  $d\underline{C}/dr$ , would not be a fan hull if locally the curve was not strictly convexly independent with respect to an endpoint. Again it has not been proved that a local break-down of the fan structure implies a global break-down.

Equation (4.1) to check for the local break-down of the fan hull would become:

$$P = \left[ (\underline{C} - \underline{C}^0) \times \frac{d\underline{C}}{dr} \right] \cdot \frac{d}{dr} \left( \frac{d\underline{C}}{dr} \right) = 0 \quad (4.3)$$

This condition is the generalized result of equation (4.1) and can be used to check if the convex hull of any reactor curve is a Fan Hull.

RESULT 27

This condition is even messier to solve algebraically for the C.S.T.R. than that for the plug flow trajectory, but it can be seen how in principle the results for the plug flow trajectory may be extended to any other reactor curve.

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### 4.4.2 The Role of C.S.T.R.'s and Differential Reactors in Forming the Boundary of the Hull

Consider if one did find that the convex hull (or sections of the hull) of the C.S.T.R. locus was a fan hull. Remembering the property that the reaction vector is collinear with the mixing vector (Result 6), it can be seen then that a plug flow reactor from the C.S.T.R. locus must extend the hull in the direction of the reaction vector. Thus the C.S.T.R. will again give bridging points, that is straight lines from a feed point to the C.S.T.R. locus, from which plug flow trajectories will start.

RESULT 28

Alternatively, the C.S.T.R. might form part of a plane or boundary of another type of face of the hull. But the mixing vector must point back to a point in the hull, and thus as the mixing vector is collinear with the reaction vector, the reaction vector must point out of the hull. Thus a plug flow trajectory will extend the hull and the C.S.T.R. will again form a bridging point.

One can also see that only a finite number of C.S.T.R.'s can lie entirely in the boundary of the attainable region. In the examples, in fact, only one locus usually lay in the boundary along the entire curve, thus forming bridging points along the whole locus. Alternatively, one might find a family of C.S.T.R.'s touching the hull at one point only (as in Section 4.7.1, Figure 4.4d).

Differential reactors, such as a Maximum Mixedness Reactor (MMR), have the property that the tangent to the curve would lie on the plane defined by the mixing and reaction vectors (from Result 2). The mixing must occur with a point that has already been achieved, and thus the mixing vector (and thus plane in which the tangent to the curve lies) must either point back into the hull or along a surface of the hull. Thus if we examine the sections of the reactor curve that lie in the boundary of the hull, we find that the reaction vector must be pointing out of the hull at these points. (This follows from Result 1 that the tangent to the curve must lie in the acute angle between the mixing and reaction vectors).

Consequently it follows that a plug flow reactor starting from the curve would extend the hull. Thus a reactor with differential reaction and mixing, would also form bridging points from which the plug flow trajectories would start and extend the hull.

RESULT 29

In both cases, if the bridging line is in the surface of the attainable region, then the reaction vector along the hull must point into the hull and become tangential at the vertex of the line, ie along the reactor curve. This is likely to be a property of the optimal reactor.

#### 4.5 Differential Reactors

When discussing a differential reactor, one must clarify how one defines the residence time along the reactor. For simplicity, we will consider a constant density system. Consider some section of the reactor of volume  $v_{in}$ , concentration  $C_{in}$  and flow rate  $M_{in}$ . We mix with a side stream of volume  $v^*$ , concentration  $C^*$  and flow rate  $M^*$ , as shown in Figure 4.1. The mixing and reaction occurs in a volume  $\Delta v$ . Thus the mass balance and the change in the outlet concentration can be described by:

$$M_{in} + M^* = M_{out} \quad (4.4)$$

$$M_{in} C_{in} + M^* C^* + R(C) \Delta v = M_{out} C_{out} \quad (4.4a)$$

Define  $q$  by:  $\frac{M^*}{\rho^*} = q \Delta v$

or in the limit, if the limit exists:  $q = \frac{d(M/\rho^*)}{dv} \quad (4.5)$

where  $\Delta v = v_{out} - (v_{in} + v^*) \quad (4.5a)$



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The residence times of the various streams are:

$$\tau_{in} = \frac{v_{in}\rho^0}{M_{in}} ; \tau^* = \frac{v^*\rho^0}{M^*} ; \tau_{out} = \frac{v_{out}\rho^0}{M_{out}} \quad (4.6)$$

The residence time of the system entering the volume element is:

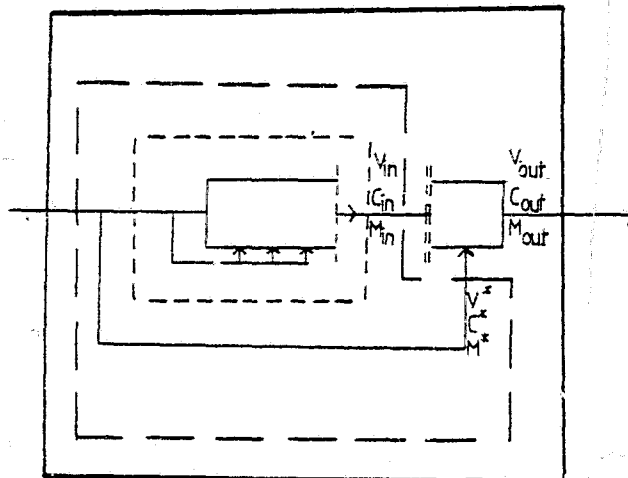
$$\tau_{system} = \frac{(v_{in} + v^*)\rho^0}{(M_{in} + M^*)} = \alpha \tau_{in} + (1-\alpha) \tau^* \quad (4.7)$$

where

$$\alpha = \frac{M_{in}}{(M_{in} + M^*)} \quad (4.7a)$$

Figure 4.1: Definition of Residence Time

- Boundary for system with space time  $\tau_{in}$
- Boundary for system with space time  $\tau_{system}$
- Boundary for system with space time  $\tau_{out}$



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The difficulty arises when one tries to define the change in residence time along the reactor, which could either be defined as  $(\tau_{out} - \tau_{in})$  or as  $(\tau_{out} - \tau_{system})$ . It seemed to me to be more consistent to use the later definition. In the limit, if the mixing is differential ie  $M^* \rightarrow 0$ , then the two definitions are the same. Using the later definition and taking the limit as  $\Delta v \rightarrow 0$ , the equation describing the differential reactor becomes:

$$\frac{dC}{dr} = q (C^* - C) + R(C) \quad (4.8)$$

Notice the similarity of this equation to equation (2.10). Further note that when  $R(C)$  and  $(C^* - C)$  are collinear and in opposite directions, then the resultant change in  $C$  can only be along the line, ie equivalent to mixing only or reaction only. If the amount mixed is in the correct proportions to counteract the reaction, ie  $q = -R(C)/(C^* - C)$ , for each component, then  $dC = 0$  and concentration in the reactor remains constant or in other words the reactors behaves as a C.S.T.R. with feed  $C^*$ . Consistent with this behaviour, the condition for  $q$  implies that  $r$  is constant in the reactor and that  $q = 1/(r - \tau^*)$ .

### 4.5.1 The Choice of Mixing Points in the Differential Reactor

The differential reactor structure, modified perhaps so that any point already achieved may be used as the mixing point, is a fairly general reactor structure. Unfortunately, it is difficult to include mixing with later points (ie back mixing) because of the problems of multiple steady states etc as discussed for the Generalized Mixing Model (GMM) (see Section 2.7.4).

When choosing a mixing point, we may consider the following questions:

- How many mixing points need one consider in a general differential reactor of the type described above?

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- Which points do you need to consider when choosing a mixing point from all the points in the hull?

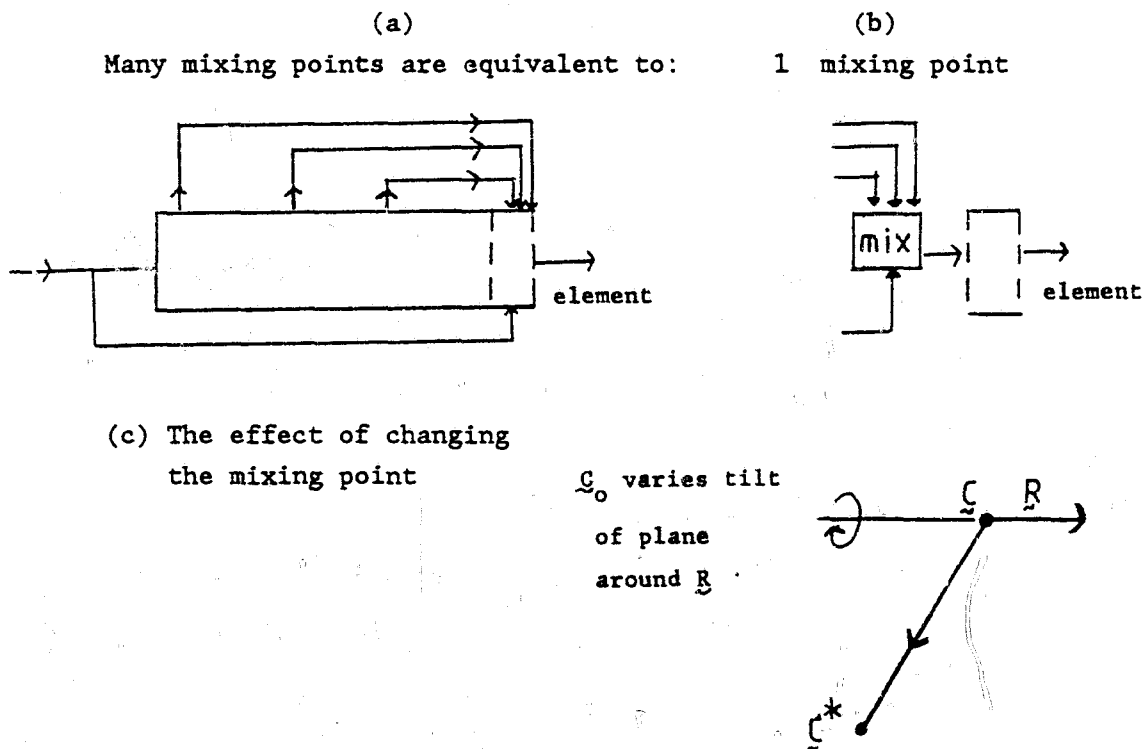
These points will be considered separately, and thereafter properties of the mixing point will be discussed.

At any point along the reactor we may add material that we already have achieved, in any proportions: for example we could have multiple feed points as shown for a section of a reactor in Figure 4.2a. However we could rather mix the side streams entering the section of the reactor first and then add them, as depicted in Figure 4.2b.

This has two important consequences, namely:

- (i) the mixing process gives us one equivalent mixing point.
- (ii) this mixing point must lie in the convex hull of all the points that we have achieved so far with the reactor.

Figure 4.2: Choosing the Mixing Point



Thus a differential reactor with only back mixing requires at most one mixing point at any point along the reactor. This point must lie in the already achieved convex hull of the reactor.

RESULT 30

Consider that we already have achieved a point somewhere along the reactor,  $\underline{C}$ , that lies in the boundary of the hull. The reaction vector at  $\underline{C}$  is  $\underline{R}$ . We must now choose a mixing point  $\underline{C}^*$  from all the points in the convex hull of the reactor, and even from all the points that we achieved by any other reactor. Geometrically,  $\underline{C}^*$  changes the tilt of the plane containing  $(\underline{C}^* - \underline{C})$  and  $\underline{R}$  (see Figure 4.2c), and the local change in concentration will lie in that plane. Thus firstly, to extend the hull as much as possible in the next element of the reactor, we must choose from the points in the hull that will tilt the plane as much as possible. This implies that the only points we need to consider must lie in the boundary of the hull - ie must be extremal points.

Thus the optimal mixing points must lie in the boundary of the hull.

RESULT 31

We wish to choose the mixing point such that the local change in the plane of  $\underline{R}$  and  $(\underline{C}^* - \underline{C})$  extends the hull as much as possible. Clearly, we must choose a mixing point such that the local changes in the differential reactor lies on the boundary of the hull. This is only possible if the plane lies in the boundary of the hull (or if  $q = 0$  or  $1/(\tau - \tau^*)$ , which we are not considering). Thus the only possible mixing points are those extremal points either directly adjacent to  $\underline{C}$  or lying on straight lines or planes formed by the extremal points connected to  $\underline{C}$  (ie forming the surface of the hull around  $\underline{C}$ )

Furthermore, as far as the geometry is concerned, we need only consider the end points of the straight lines connected to  $\underline{C}$  (and not points along the lines) as both the local change and the curvature are determined by the direction of the vector  $(\underline{C}^* - \underline{C})$  - not its magnitude. This result will be used in the proof below.

If we have a plane forming a face at  $\underline{C}$ , we can see that we need only consider:

- (i) firstly, the extremal points of the plane and

(ii) secondly, we need not consider the point that lies between  $\underline{R}$  and the other extremal points on the plane.

The proof is as follows:

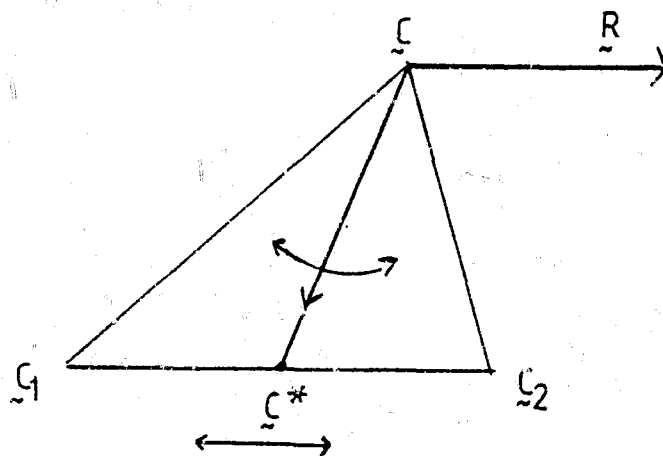
Consider Figure 4.3. A plane through  $\underline{C}$ , with extreme points  $\underline{C}_1$  and  $\underline{C}_2$ , forms part of the boundary of the attainable region at  $\underline{C}$ . As explained previously, we only need to consider end points of the lines from  $\underline{C}$  - ie points along the line  $(\underline{C}_1, \underline{C}_2)$ . This proves (i) of the above assertion.

In order for the reactor locus at  $\underline{C}$  to lie in the boundary hull, as follows from Result 29, the reaction vector  $\underline{R}$  at  $\underline{C}$  must be tangential to the surface of the hull. Thus  $\underline{R}$  must lie in the plane of  $\underline{C}$ ,  $\underline{C}_1$  and  $\underline{C}_2$ . The resultant change of concentration, which is a vector sum of  $(\underline{C}^* - \underline{C})$  and  $\underline{R}$ , will also be in the plane ie will lie between  $(\underline{C}_1 - \underline{C})$  and  $\underline{R}(\underline{C})$ . Thus we only need to consider  $\underline{C}_1$  as a possible feed point - which proves (ii) of the above assertion.

Thus the interesting result is that at most we need only consider points that are both extreme points (ie that lie in the boundary of the hull of the region) and that are also neighbouring points of  $\underline{C}$ . If there is a plane at  $\underline{C}$  that forms a face of the hull, we need only consider the point on the plane such that the angle between  $\underline{R}$  and  $(\underline{C}_{\text{plane}} - \underline{C})$  is the largest.

RESULT 32

Figure 4.3: Choice of Mixing Point from all Extremal Points



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We now divide all the extreme, neighbouring points of  $\underline{C}$  that satisfy Result 32, into two classes - firstly the neighbouring points of  $\underline{C}$  that are a differential amount away eg previous point of differential reactor curve or a point on the plug flow reactor with feed point  $\underline{C}$ ; and secondly, points that are a finite distance away, eg the feed point, equilibrium point or some other point already achieved that is important in the hull.

Points that are a differential amount away have a mixing vector that is a differential quantity while the reaction vector is of finite length. Any value of  $q$  that is not infinite, would imply only reaction or in other words a plug flow reactor. We furthermore regard an infinite  $q$  as an unacceptable choice.

Thus apart from the restrictions applied on the choice of the mixing point by Result 32, we would further require that the mixing point would have to be a finite distance away from the reaction point. This further greatly restricts the choice of mixing points and there is usually only one obvious extreme point that is connected to  $\underline{C}$  that is a candidate.

RESULT 33

### Further Properties of the Mixing Point

If we regard the properties of the hull of the attainable region, and consider the role of the differential reactor and the mixing point in forming this hull, we can consider the following cases:

(1) The mixing point  $\underline{C}^*$  is a point reached by some other reactor and  $\underline{T}(\underline{C}^*)$  is the tangent to the reactor curve at the mixing point. The points on the differential reactor locus are denoted as  $\underline{C}$ . If we make the hull of the differential reactor and mixing point (remembering that the mixing point is an extreme point of the hull and that it lies on a reactor curve), the mixing point must have the property that the tangent  $\underline{T}(\underline{C}^*)$  must also lie in the plane of  $\underline{R}(\underline{C})$  and  $(\underline{C}^* - \underline{C})$  along the whole differential reactor locus. This would require the differential reactor locus to lie in a plane, and would also require fairly odd kinetics in that the constraints on the reaction vector would be fairly severe.

RESULT 34

(ii) The mixing point  $\underline{C}^*$  varies continuously and smoothly with position in the differential reactor. This could only happen if  $\underline{C}^*$  lay on some other reactor locus that lay in the boundary of the attainable region and that was a finite distance away from the locus of the differential reactor (from Results 31 to 33). The mixing point would need to move along the reactor locus in such a manner that the tangent to the locus at the mixing point,  $\underline{T}(\underline{C}^*)$ , was in the plane of  $\underline{R}(\underline{C})$  and  $(\underline{C}^* - \underline{C})$ . (We again denote  $\underline{C}$  as a point on the locus of the differential reactor). This would be equivalent to forming the face of the hull by rolling along both curves. This is again fairly severe restrictions on the reaction vector, and this situation can not arise unless the kinetics are fairly degenerate.

RESULT 35

(iii) The mixing point is an end point, ie a feed or equilibrium point. This will be the most common situation as there is then no constraint on the direction of the reaction vector at the mixing point. This is the case that will be considered from now on, as it is only with rather degenerate kinetics (degenerate in that there must be strong dependence of the components of the reaction vector) that the first two cases will arise.

RESULT 36

If the best mixing point is a feed point, then the optimal differential reactor is a Maximum Mixedness Reactor of the type considered by Zwietering.

Thus in summary, the mixing point must lie in the boundary of the attainable region. In general it will not change with position along the differential reactor but will stay fixed, or at most, the mixing point might only change in discrete, sudden moves along the reactor. In general the mixing point will be an end point.

The role of the differential reactor in forming the boundary of the attainable region can also be inferred from the results given above. As the mixing point must be in the boundary of the hull, a finite distance away from the locus of the differential reactor and directly connected to the reactor locus, we can see the most likely, if not the only, way of fulfilling all of these requirements is if the hull of the attainable region is a fan hull between the mixing point and the locus of the differential

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reactor. Thus, at the locus, the reaction vector would be tangential to the fan hull, and, as already shown in Result 29, plug flow trajectories from the differential reactor locus would lie in the boundary of the hull. The reaction vectors along the lines making up the surface of the fan hull, would point into the hull along the lines and become tangential to the surface of the hull at the reactor locus.

RESULT 37

As shown in Result 33, the mixing point of an optimal differential reactor must lie a finite distance away from the locus of the differential reactor, and furthermore, the mixing point must be an extremal point directly connected to the reactor locus (Result 32). Thus with these restrictions, it is not possible to have a whole face of the attainable region made up of differential reactors, but rather the face will be made up of lines from the mixing point, which must be a special point in the hull, to points on the reactor locus. Thus there will only be a finite number of differential reactors that can make up the hull, and it is presumably the number of suitable mixing points that limit the number of reactor loci.

RESULT 38

This is a similar result to that obtained for C.S.T.R.'s. One might wonder if a family of differential reactors might not each touch the boundary of the region at a single point, as discussed for C.S.T.R.'s. It follows that in order for the point to lie in the boundary of the attainable region, even at just one point, the mixing point would need to be an extremal, directly connected point. (In order for a point of a curve to lie in the boundary of the attainable region, the tangent to the curve at the point must lie in the boundary. This tangent is a linear combination of the reaction and mixing vectors. The reaction vector must be tangent to the boundary and thus it follows that the mixing vector must also be tangent to the boundary.) For a family of differential reactors, this would presumably mean that the reactors would all have different feed points, and that the mixing point would be the same for all the reactors. Furthermore the mixing point would be connected to the point of the reactor that lay in the boundary of the attainable region by a fan hull. A similar structure for C.S.T.R.'s is found in Section 4.7.1, Figure 4.4d. The curve formed by the family of differential reactors in this



manner, could alternatively have been followed directly by a single differential reactor.

Thus all the results derived for a single differential reactor in the boundary of the attainable region would again apply.

#### 4.5.2 The Properties of the Optimal Differential Reactor

To simplify the notation, we will define  $\underline{V}$  as the mixing vector ( $\underline{C}^* - \underline{C}$ ). The equation describing the differential reactor is then:

$$\frac{d\underline{C}}{dr} = q \underline{V} + \underline{R}(\underline{C})$$

The optimal differential reactor will have certain properties that arise from the geometry of the reactor itself, ie out of the above equation. Furthermore, as seen in Sections 4.3.2 and 4.4, the surface of the hull of the attainable region also has geometric properties that are peculiar to it. Combined, these two sets of geometric properties should give us the properties of a differential reactor that lies in the boundary of the attainable region. These results will be compared with the analytical optimization of the differential reactor. In all the following discussions it will be assumed that the mixing point  $\underline{C}^*$  does not change with position along the differential reactor.

#### Geometric Properties of the Differential Reactor

Geometrically, the best differential reactor is the one which extends the hull the most. In other words, we wish to chose  $q$  so as to move the curve of the differential reactor out of the current hull as much as possible. Consider the problem geometrically. Assume we have achieved a concentration  $\underline{C}$ . We allow mixing with various amounts of some  $\underline{C}^*$  (chosen using

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Results 31 to 36). Locally the reactor trajectory must move in the plane formed by the mixing vector  $\underline{V}$  and the reaction vector  $\underline{R}$ . Varying  $q$  varies the direction of movement in this plane.

What we want is to find the value of  $q$  which moves the differential reactor curve furthest out of the plane ie the one with the largest curvature in the direction perpendicular to the plane.

Define arc length  $s$  of a curve as:

$$\frac{ds}{dr} = \left| \frac{d\underline{C}}{dr} \right| \quad (4.9)$$

The unit tangent  $\underline{T}$  to the curve of the differential reactor is then:

$$\underline{T} = \frac{d\underline{C}}{ds} = \frac{d\underline{C}}{dr} \times \frac{dr}{ds} = \frac{1}{\left| \frac{d\underline{C}}{dr} \right|} \times \frac{d\underline{C}}{dr} \quad (4.10)$$

The Curvature of the curve is:

$$\frac{d\underline{T}}{ds} = \frac{d\underline{T}}{dr} \times \frac{dr}{ds} = \frac{1}{\left| \frac{d\underline{C}}{dr} \right|^2} \times \frac{d^2\underline{C}}{dr^2} \quad (4.11)$$

We wish, however, to find the differential reactor curve with the largest curvature away from the normal to the plane (defined by the reaction vector  $\underline{R}(\underline{C})$  and the mixing vector  $(\underline{C}^* - \underline{C}) = \underline{V}$ ), ie:

$$\text{maximize: } J = \left( \frac{d\underline{T}}{ds} \right) \cdot (\underline{V} \times \underline{R}(\underline{C})) \quad (4.12)$$

$$\text{or maximize: } J = \frac{1}{\left| \frac{d\underline{C}}{d\tau} \right|^2} \left( \frac{d^2 \underline{C}}{d\tau^2} \right) \cdot (\underline{V} \times \underline{R}(\underline{C})) \quad (4.12a)$$

The above expression simplifies, using the result:

$$(\underline{A} \times \underline{A}) \cdot \underline{B} = \underline{A} \cdot (\underline{A} \times \underline{B}) = 0 \quad \text{to:}$$

$$J = \frac{(\underline{qV} + \underline{R}(\underline{C})) \underline{VR} \cdot (\underline{V} \times \underline{R}(\underline{C}))}{\left| \frac{d\underline{C}}{d\tau} \right|^2} \quad (4.13)$$

where

$$(\underline{AVB})_j = \sum_i (A_i \frac{\partial B_j}{\partial C_i}) \quad (4.13a)$$

Rather than continue with the differentiation of equation (4.13), we shall rather firstly consider the geometric properties of the surface of the attainable region.

#### The Geometric Properties of the Boundary of the Attainable Region

The role of the optimal differential reactor in the structure of the hull of the attainable region was summarized in Result 37. To recap,  $\underline{C}^*$ , the mixing point, is an important point in the hull. We expect to find lines (ie the mixing vectors) sweeping out a surface from this point to the optimal differential reactor curve trajectory. Along the lines we expect to find that as we move from the mixing point towards the reactor locus, the reaction vectors point into the hull and eventually become tangential to the surface at the reactor locus. This is mathematically equivalent to requiring that the change in the reaction vector in

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the direction of the mixing vector lies in the plane of  $\underline{R}(\underline{C})$  and  $\underline{V}$  at  $\underline{C}$ , or:

$$S = \underline{V} \cdot \underline{V} \times \underline{R}(\underline{C}) = 0 \quad (4.14)$$

An alternative way of visualizing the geometrical interpretation of the above equation is as follows: consider the family of plug flow reactors in the space of the attainable region. Now consider in particular the plug flow trajectories that pass through the line of the fan hull between the mixing point  $\underline{C}^*$  and the boundary of the fan hull at  $\underline{C}$ . The plug flow trajectories that intersect the line near  $\underline{C}^*$  must move into the region and stay inside the region. As the intersection point moves towards  $\underline{C}$ , so the trajectories must lie closer and closer to the boundary of the attainable region. The trajectory of the plug flow reactor that just touches  $\underline{C}$  defines the boundary of the attainable region (from  $\underline{C}$  onwards along its trajectory). Thus in the neighbourhood of  $\underline{C}$ , the family of plug flow trajectories must be tangential to the boundary of the attainable region. If we extend the line beyond  $\underline{C}$ , we find that the plug flow trajectories that intersect the line in this region, always remain outside the attainable region. The planes of the fan hull thus define the tangent planes to a family of plug flow trajectories.

Equation (4.14) describes a surface on which the three vectors are coplanar. The optimal differential reactor locus must lie in or, in other words, move along this surface. In order for the locus to move along the surface, the plane in which the reactor moves locally, that is the plane defined by  $\underline{R}(\underline{C})$  and  $\underline{V}$ , must be tangential to the surface if the resulting motion is to lie in the surface. The normal vector to the surface  $\underline{N}$ , is defined as  $\underline{V} \times \underline{R}$ . Thus the locus of the optimal differential reactor, in the surface  $S$ , must be defined by:

$$\underline{N} \times (\underline{V} \times \underline{R}) = 0 \quad (4.15a)$$

or equivalently:

$$\underline{N} \cdot \underline{R} = 0 \quad \text{and} \quad \underline{N} \cdot \underline{V} = 0 \quad (4.15b)$$

Equations (4.14) and (4.15a & b) would together define the differential reactor that lies in the boundary of the attainable region.

The question now arises how does this compare with equation (4.13), where the optimal reactor was defined in terms of curvature? If the results of equation (4.14) are used; ie  $\underline{R}(C)$ ,  $\underline{V}$  and  $\underline{VVR}$  are all coplanar; differentiating equation (4.13) with respect to  $q$  and simplifying, gives:

$$\left[ \frac{dC}{dr} \cdot \underline{V} \right] \left[ \underline{RVR} \cdot (\underline{V} \times \underline{R}) \right] = 0 \quad (4.16)$$

The above result assumes that we are not at a solution of a C.S.T.R. ie  $|dC/dr| \neq 0$ .

This implies that either:

- $\underline{RVR}$  lies in the plane of  $\underline{R}$  and  $\underline{V}$ , or else that
- $q$  must be chosen such that  $dC/dr$  is perpendicular to the mixing vector  $\underline{V}$ .

The first condition will only hold for kinetics that are very degenerate in that all four vectors;  $\underline{R}$ ,  $\underline{V}$ ,  $\underline{RVR}$  and  $\underline{VVR}$ ; are all coplanar along a region of space. This could perhaps happen if one of the components of the reaction vector was a linear combination of the other two components, such as occurs with temperature as a variable. In this case as the change in the direction in the reaction vector in the direction of both  $\underline{R}$  and  $\underline{V}$  is in the plane of  $\underline{R}$  and  $\underline{V}$ , it would seem that not only the local, but also the global motion of the differential reactor must lie in a plane. This agrees with the results of equation (4.15), in that if all four vectors are coplanar, then  $J = 0$  or in other words, the curvature is zero and the curve lies in a plane.

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The second condition could apply if the angle between the reaction vector and the mixing vector was greater than 90°.

To decide which of these two conditions is the correct one, or indeed whether both conditions are possible, we must see how these results compare to those derived from the geometric properties of the attainable region, ie the results of equations (4.14) and (4.15).

Using the fact that  $\underline{R}$ ,  $\underline{V}$  and  $\underline{VVR}$  are coplanar, equation (4.15) simplifies to:

$$\underline{V} \cdot \underline{N} = 0 = \underline{V} \cdot [ \underline{V} \cdot \nabla ( \underline{R}_x(\underline{VVR}) ) ] \quad (4.17)$$

$$\underline{R} \cdot \underline{N} = 0 = \underline{R} \cdot [ \underline{V} \cdot \nabla ( \underline{R}_x(\underline{VVR}) ) + \underline{V}_x(\underline{V}_x(\underline{R}_x(\underline{VVR}))) ] \quad (4.18)$$

Solving equation (4.17) results in a three dimensional tensor, and rather than writing the equation in tensor form, we will revert to the more usual notation.

$$R_k^{ij} = \frac{\partial^2 R_k}{\partial C_i \partial C_j}$$

Using this notation, and that  $(\underline{V}_x \underline{R})_k$  is the k-th component of the vector  $(\underline{V}_x \underline{R})$ , equation (4.17) becomes:

$$\sum_k ( \sum_j \sum_i V_j V_i R_k^{ij} ) ( \underline{V}_x \underline{R} )_k = 0 \quad (4.19)$$

Similarly, equation (4.18) simplifies to:

$$-(1+\beta)(\underline{VVR}) \cdot (\underline{V}_x \underline{R}) + \sum_k ( \sum_j \sum_i R_j V_i R_k^{ij} ) ( \underline{V}_x \underline{R} )_k = 0 \quad (4.20)$$

where  $\beta$  is defined by:

$$\underline{VVR} = \alpha \underline{V} + \beta \underline{R} \quad (4.20a)$$

Using the results of the geometric properties of the differential reactor, if  $\underline{R}$ ,  $\underline{V}$  and  $\underline{RVR}$  are coplanar; as follows from equation (4.16); then equation (4.20) simplifies to:

$$\sum_k \left( \sum_j \sum_i R_j V_i R_k^{ij} \right) (\underline{V} \times \underline{R})_k = 0 \quad (4.21)$$

Notice the similarity between equations (4.19) and (4.21). Thus regions in space where both these equations were true, would presumably be solutions of a differential reactor that lay in the boundary of the attainable region. This condition may not be the only condition when a differential reactor lay in the boundary of the attainable region, as one could presumably also have that equations (4.19) and (4.20) together with the other condition of equation (4.16), ie that  $\underline{V}$  and  $d\underline{C}/d\tau$  were perpendicular, as well. Rather than elaborate now on these two results, the analytical optimization of a differential reactor will first be discussed, and the similarity between the geometrical and analytical results examined.

#### Analytical Optimization of a Differential Reactor

Remembering that we can write the equations describing reaction in terms of a scalar variable, which we usually regarded as  $\tau$ , we will now return to the notation introduced in equation (2.8) and write the equations rather in terms of the positive, scalar quantity  $\varphi$ , which has units of time. This is done so as to generalize the analysis given below so that it will hold for all three dimensional coordinate systems, including those with space time as a variable.

We are given:

$$\frac{d\underline{C}}{d\varphi} = q (\underline{C}^* - \underline{C}) + \underline{R}(\underline{C}) = q\underline{V} + \underline{R}(\underline{C})$$

where if component  $i$  of  $\underline{C}$  is space time,  $R_i$  is 1. We wish to find  $q(\varphi)$  such that  $\underline{C}$  takes on an extreme value some value  $\varphi_F$ .

The Hamiltonian H is defined as:

$$H = \underline{Z} \cdot \frac{dC}{d\varphi} = \underline{Z} \cdot (q\underline{V} + \underline{R}) = 0 \quad (4.22)$$

where  $\underline{Z}$  is the adjoint vector. The value of  $\varphi$  is not fixed, but can take on its optimal value, thus  $H=0$ . Furthermore:

$$\frac{dH}{dC_i} = \frac{dZ_i}{d\varphi} = qZ_i - \sum_j Z_j \frac{dR_j}{dC_i} \quad (4.23)$$

and

$$\frac{dH}{dq} = \underline{Z} \cdot \underline{V} = 0 \quad \text{for singular control} \quad (4.24)$$

Using this result in equation (4.22), we find that  $\underline{Z} \cdot \underline{R} = 0$ . Furthermore:

$$\frac{d}{d\varphi} \left( \frac{dH}{dq} \right) = 0 = - \underline{Z} \cdot \underline{VVR} \quad (4.25)$$

Thus equations (4.22) to (4.24) give us that  $\underline{Z}$  dotted with  $\underline{R}$ ,  $\underline{V}$  or  $\underline{VVR}$  is 0, or in other words, all three vectors are coplanar. This is the same result as we obtained from the geometry of the attainable region, ie equation (4.14).

If we differentiate the above equation again, we find that:

$$\frac{d^2}{d\varphi^2} \left( \frac{dH}{dq} \right) = 0 = \underline{Z} \cdot (\underline{VVR})\underline{VR} - \underline{Z} \cdot \frac{d}{d\varphi} (\underline{VVR}) \quad (4.26)$$



This equation simplifies to:

$$(1+\beta) \underline{Z} \cdot \underline{RVR} - \underline{Z} \cdot \left[ \sum_i \sum_k V_i R_k^{ij} (qV_j + R_j) \right] = 0 \quad (4.27)$$

where  $k = 1, \dots, 3$ , and  $\beta$  and the other terms are defined as before. Remembering that  $\underline{Z}$  is perpendicular to both  $\underline{V}$  and  $\underline{R}$  (from the results of equations (4.23) and (4.24)), the direction of  $\underline{Z}$  is in the same direction as  $(\underline{V} \times \underline{R})$ , or  $(\underline{R} \times \underline{V})$ . The orientation is not important, and we may write:

$$\underline{Z} = \gamma (\underline{V} \times \underline{R}) \quad \text{where } \gamma \text{ is some scalar quantity} \quad (4.27a)$$

and thus

$$(1+\beta) \underline{RVR} \cdot (\underline{V} \times \underline{R}) - \sum_k \sum_j \sum_i \left[ V_i R_k^{ij} (qV_j + R_j) (\underline{V} \times \underline{R})_k \right] = 0 \quad (4.28)$$

Notice the similarity in this result and that obtained from geometric considerations. Thus, if the conditions stated in the geometric proof are valid, i.e. that the four vectors  $\underline{R}$ ,  $\underline{V}$ ,  $\underline{RVR}$  and  $\underline{VVR}$  are coplanar and equations (4.19) and (4.20) are true; then above equation will also be true. Which is the more general condition is not certain, but it is suspected that the above equation does not take into account the properties of the attainable region, that is, that it is not as general as those obtained by the geometric arguments.

RESULT 39

It would also seem that the second condition, that is  $(dC/d\underline{V}=0)$ , obtained from geometric arguments is too restrictive. This condition is not understood and has not been further examined.

4.6 Further Properties of the Surface of the Attainable Region

One must differentiate between the hull of a reactor curve and that of the complete attainable region. In this section, the surface of the attainable region will be considered and the some of the properties of the surface will be deduced.

It was shown (Conjecture 2.2 of Section 2.10) that all points along a reactor locus that lies in the boundary of the attainable region must be reached by some reaction, ie the reaction vector must be a component of the tangent vector to a reactor locus. This component is the only component that can move the reactor locus out of the existing hull, in that it is responsible for moving the locus in a direction different to that of the mixing component, which because of the convexity of the hull, points into the hull. No reaction vector along a reactor locus that lies in the boundary of the attainable region can point into the region.

RESULT 40

Thus this has two consequences for a reactor locus (excluding plug flow trajectories) that lies in the boundary of the attainable region. Firstly, plug flow reactors off the reactor curves must always extend the hull, as these trajectories move in the direction of the reaction vector. Secondly, the reaction vectors along the reactor curve can either point out of the hull or be tangential to the hull. If the reaction vectors along the reactor curve point out of the hull, the plug flow trajectories off the curve will extend the hull and the curve will therefore lie inside the hull, which contradicts our assertion that the reactor curve lay in the boundary of the region. Thus the only possibility is that for any reactor locus in the boundary of the hull, the reaction vectors along the curve must be tangential to the hull, so that the plug flow reactors lie in the boundary of the hull in the neighbourhood of the curve. Thus Results 26 and 27 can be extended, so that not only the tangent to the curve is considered, but also the reaction vector. This does not add any additional constraints to the choice of the differential reactor, as this result is always true in this case; it could however affect the optimization of some other type of reactor.

RESULT 41

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Alternatively, if one considers the support planes that form the faces of the attainable region, the reaction vectors along the reactor curves that form the edges of the hull, must lie in the support planes forming the surface of the attainable region.

Consider furthermore that this reactor curve that lies in the boundary of the attainable region, forms the surface of the attainable region in such a way that it forms a fan hull with some point  $C^*$ . The same argument that was used to derive equation (4.14) will again hold, and thus the surface along which any reactor curve in the boundary of the attainable region lies, and which forms a fan hull with some point  $C^*$ , will be described by equation (4.14). This condition will also describe any curve (even if it is formed by a family of trajectories or reactor curves), that lies in the boundary of the attainable region, if the curve has plug flows leaving it tangentially and if it forms a fan hull with some point  $C^*$  in the boundary of the region. This type of structure can be seen in Section 4.9.1 Fig. 4.10a.

Notice also that the C.S.T.R. locus, with feed point  $C^*$  or in other words from the origin of the fan, always satisfies equation (4.14). Thus the C.S.T.R. moves in this surface, and the C.S.T.R. locus will always have a family of plug flow trajectories leaving it tangentially. This agrees with Result 20 which was derived from properties of the reactor itself. Thus the bridging properties of the C.S.T.R. and the differential reactors are applicable to any reactor curve (excluding a plug flow trajectory) or family of curves, that lies in the boundary of the attainable region.

When finding the hull of a reactor locus that lies in the boundary of the attainable region, not only must one bear the results of Section 4.4 in mind (ie with regards to the tangent to the curve), but one should also remember that the above results implies certain restrictions on the reaction vector along the curve.

The likelihood that some point other than an end point (as discussed in Section 4.5.1) being the mixing point for a differential reactor that lies in the boundary of the hull is

also further restricted that the reaction vector at the mixing point,  $\underline{R}(C^*)$ , must lie in the plane of the mixing and reaction vectors  $\underline{R}(C)$  and  $(C^* - C)$ .

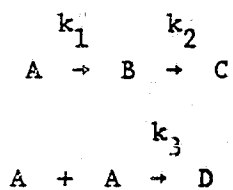
RESULT 42

At this stage, some examples to illustrate the method of constructing the attainable region in three dimensions will be presented. The conclusions reached above will be referred to and it will be shown how they apply. Any other results that come from the example will be noted and the general implications will be discussed in Section 4.12.

#### 4.7 Examples in Three Dimensional Concentration Space

##### 4.7.1 Example 10: Van de Vusse Kinetics

The Van de Vusse kinetics are:



Define  $x = (\text{concentration A}) / (\text{initial concentration of A})$

$y = (\text{concentration B}) / (\text{initial concentration of A})$

$z = (\text{concentration D}) / (\text{initial concentration of A})$

$w = (\text{concentration C}) / (\text{initial concentration of A})$

$a_1 = k_3/k_1 * (\text{initial concentration of A})$

$a_2 = k_2/k_1$

$$\text{Thus } r_x = -x - a_1 x^2 \quad (4.29a)$$

$$r_y = x - a_2 y \quad (4.29b)$$

$$r_z = 0.5 a_1 x^2 \quad (4.29c)$$

$$r_w = a_2 y \quad (4.29d)$$

The previous work done on these kinetics is discussed in Section 1.4.1 and the example was previously done in two dimensional x-y space (see Section 3.2.1 Example 1). It was found that for  $a_1 = a_2 = 1$  the plug flow trajectory was best in x-y space. When  $a_1 = 20$ , however, the the plug flow trajectory was concave and the C.S.T.R. extended the hull. In three dimensional space one finds, using equation (4.1) that the plug flow trajectory is strictly convex. The third component thus reduces the linear dependence exhibited by the plug flow trajectory when  $a_1 > a_2$ , and the behaviour exhibited is now similar (in that the structures forming the faces of the attainable region are the same) for all values of  $a_1$ . We can consider the behaviour of the system in either x-y-z space or x-y-w space. In one case we will use  $a_1=1$  and in the other  $a_1=20$  to show how the behaviour of the plug flow trajectory is affected by this coefficient in three dimensional space. We will consider each example separately.

#### The Attainable Region in x-y-z Space; $a_1=20; a_2=1$

The rate vector is only dependent on two of the concentrations, namely x and y and should therefore show simple behaviour over a region in concentration space. Note that the component of the rate vector in the z-direction varies only with value of x and not y or z.

The completed attainable region is shown in Figure 4.4a, and the following colours were used:



Figure 4.4a: The Attainable Region for Van de Vusse Kinetics in x-y-z space

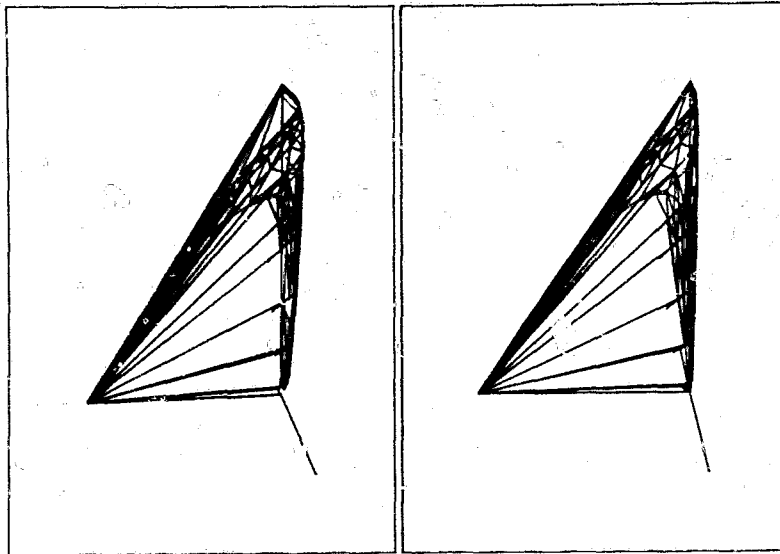


Figure 4.4b: Hull of the feed plug flow trajectory

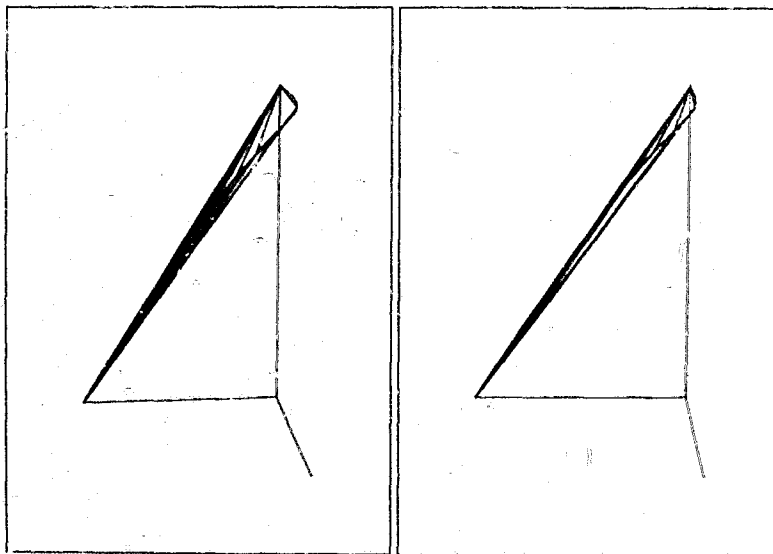


Figure 4.4c: Hull with the feed C.S.T.R. included

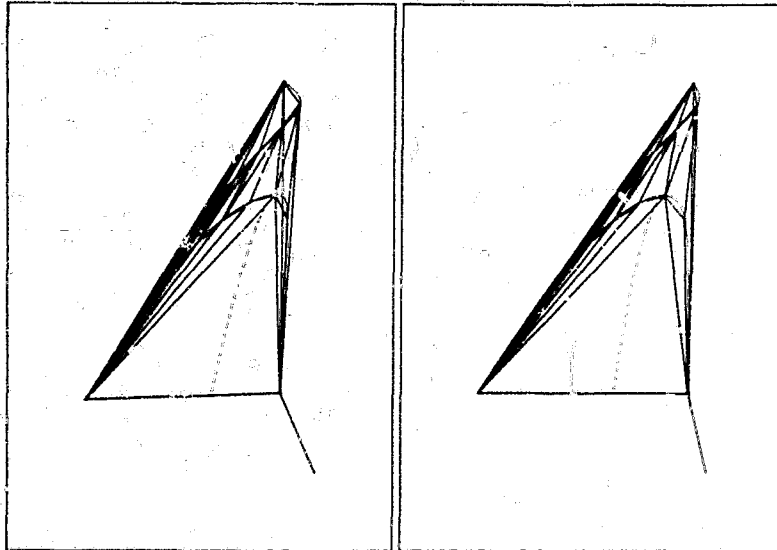
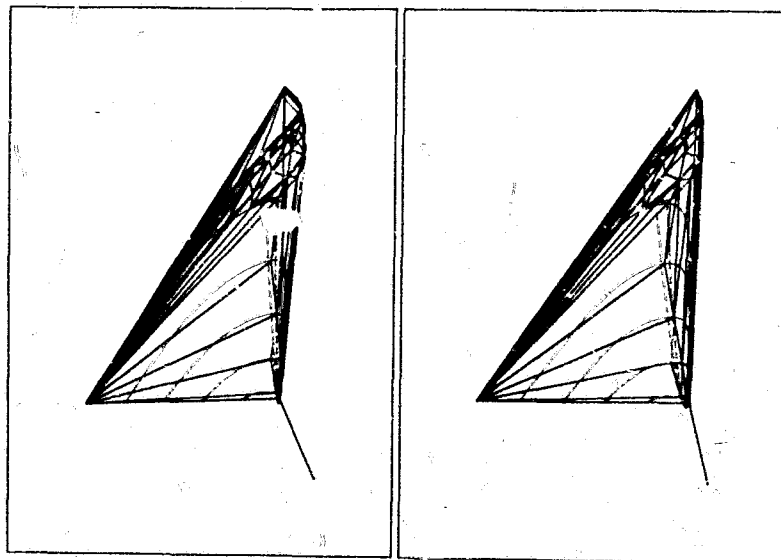


Figure 4.4d: Hull with the extra C.S.T.R.'s drawn in





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To test where the rate vectors points outwards one uses:

$$[\underline{R}(\underline{C}) \times (\underline{C}^* - \underline{C})] \cdot \underline{R}(\underline{C}^*) = 0 \quad (4.30)$$

where

$$\underline{C}^* = \alpha \underline{C} + (1-\alpha) \underline{C}^0 \quad \text{and} \quad 0 \leq \alpha \leq 1$$

and  $\underline{C}$  is a point on the plug flow trajectory

$\underline{C}^0$  is the feed or equilibrium point.

$\underline{C}^*$  is a point on the fan

Step 2:

As the rate vectors point out from the feed point onwards, it is most likely that the C.S.T.R. locus from the feed point will extend the hull. This agrees with our intuition from the two dimensional example. The C.S.T.R locus from the feed point is drawn in on on Figure 4.4c and the convex hull of the new enlarged attainable region is shown. Notice the structure of the boundary of the attainable region. It consists of :

- (a) the fan from the plug flow equilibrium point to the plug flow trajectory, which is part of the fan structure of the hull of the plug flow trajectory.
- (b) fan structures between both the C.S.T.R. equilibrium and feed points and the C.S.T.R. locus.
- (c) a plane between the feed point, the C.S.T.R. equilibrium point and a point on the C.S.T.R. locus.
- (d) a curved surface between the plug flow trajectory and the C.S.T.R. locus.

The direction of the rate vector along the C.S.T.R. locus is easily visualized over the section of the fan hull from the feed point, as by definition the rate vector is collinear with the line forming the fan. Thus over this section of the C.S.T.R. locus the plug flow trajectories will extend the hull. The last point of the fan, denoted  $\underline{C}$  for ease of reference, has the interesting property that it defines the extreme position of the plane between the feed point, the C.S.T.R. equilibrium point and the C.S.T.R. locus. The point  $\underline{C}$  is defined as the point on the

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C.S.T.R. locus where the tangent  $\underline{T}(\underline{C})$ ,  $(\underline{C}-\underline{C}_f)$  and  $(\underline{C}-\underline{C}_e)$  are coplanar. This point does not correspond to point  $\underline{C}$  of Figure 3.3, and in fact the point  $\underline{C}$  that is found as described above, would lie on the C.S.T.R. locus after point  $\underline{C}$  of Figure 3.3.

The rate vectors still point outwards over regions of the plane described in (c) above, from the green dotted line to the equilibrium point and over the curved surface described in (d).

### Step 3:

More C.S.T.R.'s are drawn in with feeds along the base of the plane, ie along the line between the feed point and the C.S.T.R. equilibrium point. These extend the hull as shown in Figure 4.4d by a fan structure. The curve through the points marked by the red dotted line is described as the points where a plane through the feed point is tangent to the family of C.S.T.R.'s. This curve does not lie in the surface described by equation (4.14), and thus the rate vector is not tangent to the fan structure along the red dotted line. This can be seen from the geometry of the situation, as the vector from the point on the C.S.T.R. to the feed point lies inside the hull. Thus the rate vector must point out of the region. The edge of the fan structure does not exactly agree with the dotted line due to numerical error as only a finite number of points are used to construct the hull.

The green dotted line represents the curve along which the rate vectors on the fan structure are tangential. It happens to be very close to the edge of the fan structure, presumably as the fan structure is not too curved.

### Step 4:

Plug flow trajectories starting on the green dotted line, that is where the rate vector is tangential to the fan structure, are drawn in. Plug flows starting on the C.S.T.R. locus are also added hull of the attainable region is extended as shown in Figure 4.4a.

The plug flow trajectories that start on the feed C.S.T.R. locus extend the hull. However, one of these trajectories extends the region the most in the x-y plane, and the plug flow trajectories after this lie inside the hull as shown. The plug flow trajectory that extends the hull in the x-y plane corresponds to that found in the two dimensional example, and its feed point on the C.S.T.R. locus corresponds to point C of Figure 3.3. The plug flow trajectories that start on the fan structure extend the hull in a different direction as seen in the figure.

It is interesting to mention here that when the values of  $a_1 = a_2 = 1$  are used, the structure of the hull is very similar, except that the plug flow trajectories off the C.S.T.R. locus lie inside the feed plug flow trajectory in the projection into x-y space.

It is worth pointing out the role of the C.S.T.R. locus in forming the boundary of the attainable region. Only the feed C.S.T.R. lies in the boundary and the plug flow trajectories leave this locus tangentially. This agrees with Result 28. The other C.S.T.R.'s that were used to construct the hull lie inside the attainable region and do not actually form the boundary. This behaviour will be discussed later in Section 4.11.

#### The Attainable Region in x-y-w Space; $a_1=1; a_2=1$

The completed attainable region is shown in Figure 4.5, and the following colours were used:

The axes are as follows:

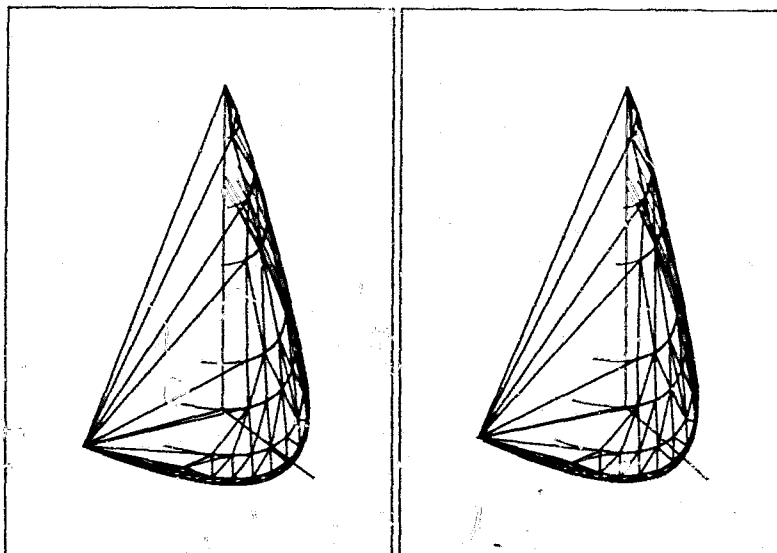
x = Blue	Range 0 to 1
y = Red	Range 0 to 0.22
w = Green	Range 0 to 1

Plug flow trajectories are drawn in blue and C.S.T.R.'s in red. The planes and lines forming the faces of the attainable region are drawn in black.

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The structure of the hull is very similar to that discussed above, and so will not be discussed in detail again. Only the completed attainable region is shown and not the individual construction steps. Basically, it is found that the hull of the feed plug flow trajectory is a fan hull, with rate vectors pointing outwards over sections of the feed fan of the hull. The feed C.S.T.R. locus is drawn in and the same structures that are mentioned in Step 2 of the previous example are present again (the C.S.T.R. introduces a new equilibrium point again). If further C.S.T.R.'s with feed points on the line between the feed point and the C.S.T.R. equilibrium point are included they extend the hull in a similar manner to that described previously. The rate vector still points outwards over the fan structure formed by the tangent planes to the C.S.T.R.'s. and also over a section of the fan structure with the C.S.T.R. locus from the feed point. Plug flow trajectories with feed points where the rate vector is tangent to the surface of the fan structures and from the feed C.S.T.R. extend the region and form the boundary of the attainable region as shown in Figure 4.5.

Figure 4.5: The Attainable Region for Van de Vusse Kinetics in x-y-w space



Notice how the projections of the plug flow trajectories in the x-y plane lie inside that of the feed plug flow trajectory. This is as one would expect from the results of the two dimensional examples done in previously in Section 3.2.1.

#### 4.7.2 Example 11: First Order Kinetics

First order or linear kinetics have been considered in general before (a discussion on the previous work on this is given in Section 1.4.3). A specific example to show the geometric properties of first order kinetics will firstly be constructed. Thereafter it will be shown how many of the previous results found by traditional optimization methods can be explained and interpreted much more easily from the geometric properties of the attainable region.

The following system of first order reactions was considered:



The values of the rate constants are shown above the reaction arrows. This system of reactions depends on the concentrations of four components. The mass balance constraint, however, relates one of the concentrations to the other three concentrations and thus there are only three independent variables. In this example the concentrations of A, B and D were chosen as the independent variables.

Define  $x = (\text{concentration of A}) / (\text{Concentration of pure A})$   
 $y = (\text{concentration of B}) / (\text{Concentration of pure A})$   
 $w = (\text{concentration of D}) / (\text{Concentration of pure A})$

The attainable region for a feed point of pure A, ie  $x=1$  and  $y=w=0$ , was drawn in x-y-w concentration space and is shown in Figure 4.5.



The behaviour of the rate vector on the surface of the attainable region is very interesting. The properties of the rate vector can best be examined by looking at the behaviour of the family of plug flow reactors. On the feed fan of the feed plug flow trajectory, the plug flow trajectories would move into the attainable region (not shown) as the rate vector points inwards on this fan. On the equilibrium fan, the plug flow trajectories which start on the line between the feed and equilibrium points, lie entirely on the fan-shaped surface (as shown) i.e. the rate vectors are tangential to this face. The other plug flow trajectories (those which do not have feed points on the feed-equilibrium line) never leave the attainable region after entering it. This example is thus a geometric interpretation of the known result that for linear kinetics, a plug flow reactor is always optimal. A geometric proof of this result is given below.

### First Order Kinetics in $R^3$

Consider the following general linear kinetics given by:

$$\frac{d\underline{C}}{d\tau} = \underline{R}(\underline{C}) = \underline{A} \underline{C} \quad \underline{C}(\tau=0) = \underline{C}_f^0 \quad (4.31)$$

where  $\underline{C}$  is the concentration vector and  $\underline{A}$  the rate matrix.

The solution of the plug flow trajectory is:

$$\underline{C} = e^{\underline{A}\tau} \underline{C}_f^0 \quad \text{for } \tau \geq 0 \quad (4.32)$$

The proof consists of three parts, firstly to show that the points on the trajectory are extremal, secondly to show that the hull is a fan hull and lastly, to show that no rate vectors point outwards. Each section of the proof is done separately.

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To Prove: The points of the plug flow trajectory are all extremal points.

Proof: If the points along the plug flow trajectory are all extremal points, this is equivalent to the points on the trajectory all being convexly independent.

To show that the points are convexly independent, we wish to show that:

$$\underline{C}(r) = \sum_{\text{all } i} \mu_i \underline{C}(r_i) \quad \mu_i > 0 \text{ and } \sum_{\text{all } i} \mu_i = 1 \quad (4.33)$$

In other words, we must prove that:

$$e^{Ar} \underline{C}_f^o = \sum_{\text{all } i} \mu_i e^{Ar_i} \underline{C}_f^o \quad (4.34)$$

where  $\mu_i > 0$  and  $\sum_{\text{all } i} \mu_i = 1$

The proof was provided by Professor C. M. Crowe and is given in Appendix 2.

To Prove: That the convex hull of the plug flow trajectory is a fan hull.

Proof: Rather than use equation (4.1) which was derived for a local break down of the fan hull, and which has not been shown to be sufficient, we will rather show globally that the fan structure cannot break down. The conditions under which the fan structure breaks down is when the function is not strictly convex, or equivalently if two points and the two corresponding rate vectors lie in a plane.



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We wish to show that if:

$$\underline{a} \cdot \underline{C}_1 = \zeta \quad , \quad \underline{a} \cdot \underline{C}_2 = \zeta$$

$$\text{and } \underline{a} \cdot A \underline{C}_1 = 0 \quad (4.35)$$

$$\text{then } \underline{a} \cdot A \underline{C}_2 \neq 0$$

where  $A$  is the rate matrix,  $\underline{a}$  is a vector,  $\zeta$  is a scalar and  $\underline{C}_1$  and  $\underline{C}_2$  lie on the plug flow trajectory.

This proof was again given by Professor C.M. Crowe, and the proof is given in Appendix 3.

Thus the convex hull of any plug flow trajectory with linear kinetics will be the fan hull.

To Prove: The rate vector does not point out of the fan hull.

Proof: Let us look firstly at the equilibrium fan described by:

$$\sum_{\text{all } i} \mu \underline{C}_e^0 + (1-\mu) \underline{C}_i \quad 0 \leq \mu \leq 1 \quad (4.36)$$

where  $\underline{C}_i$  satisfies the plug flow trajectory and  $\underline{C}_e^0$  is the equilibrium point.

The rate vector at some point  $\underline{C}^*$  on the hull is described by:

$$\begin{aligned} \underline{R}(\underline{C}^*) &= A (\mu \underline{C}_e^0 + (1-\mu) \underline{C}_i) \\ &= (1-\mu) A \underline{C}_i \end{aligned} \quad (4.37)$$

The rate vector is thus tangent at the point  $\underline{C}_i$  and thus is always tangent to this face of the hull. This face of the hull is

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made up of the family of plug flow reactors with feed points on the  $(\underline{C}_f^0 - \underline{C}_e^0)$  line, where  $\underline{C}_f^0$  refers to the feed point. This can be shown by considering a plug flow reactor with a feed point on this line ie:

$$(\mu \underline{C}_f^0 + (1-\mu) \underline{C}_e^0).$$

The solution of the plug flow trajectory is given by:

$$\begin{aligned} \underline{C}(\tau) &= e^{A\tau} (\mu \underline{C}_f^0 + (1-\mu) \underline{C}_e^0) \\ &= \mu e^{A\tau} \underline{C}_f^0 + (1-\mu) e^{A\tau} \underline{C}_e^0 \end{aligned} \quad (4.38)$$

Using the series expansion for  $e^{A\tau}$  the term on the right hand side becomes:

$$\underline{C}(\tau) = \mu e^{A\tau} \underline{C}_f^0 + (1-\mu) \underline{C}_e^0 \quad (4.38a)$$

From this it can be seen that the plug flow trajectory from a feed point on the  $(\underline{C}_f^0 - \underline{C}_e^0)$  line is a linear combination of the original feed trajectory and the equilibrium point.

Now let us look at the face made up by the feed fan ie:

$$\sum_{\text{all } i} \mu \underline{C}_f^0 + (1-\mu) \underline{C}_i$$

The rate vector at some point  $\underline{C}^*$  of the face is given by:

$$\begin{aligned} \underline{R}(\underline{C}^*) &= A(\mu \underline{C}_f^0 + (1-\mu) \underline{C}_i) \\ &= \mu A \underline{C}_f^0 + (1-\mu) A \underline{C}_i \end{aligned} \quad (4.39)$$

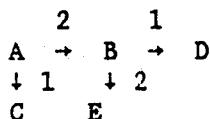
The second term on the right hand side is a vector that is tangent to the surface and the first component points into the hull when  $\mu=1$  (as it points in the direction of the plug flow trajectory) and it must therefore point into the hull for all  $\mu$ .

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By proving the above, we have shown that for linear kinetics, the plug flow trajectory defines all possible concentrations that can be reached by mixing and reaction using geometric ideas only.

### 4.7.3 Example 12: Denbigh Kinetics

The Denbigh reaction is as follows:



The numbers next to the arrows indicate the order of reaction.

We wish to find the attainable region in terms of concentration of A, B and D. Previous work on these kinetics is discussed in Section 1.4.4. The same values of the reaction constants and feed concentration that were used by Chitra and Govind (1985a) are used in this example. Chitra and Govind wished to determine the maximum amount of D that could be produced at a 95% conversion of A. They found a serial combination of plug flow and C.S.T.R. to be optimal and the maximum concentration of D was found to be 2.92 mol/l.

Define  $x = (\text{Concentration A})/(\text{Initial Concentration of A})$

$y = (\text{Concentration B})/(\text{Initial Concentration of A})$

$z = (\text{Concentration D})/(\text{Initial Concentration of A})$

The rates of reaction are:

$$r_x = -x^2 - 0.1x \quad (4.40a)$$

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$$r_y = x^2 - 0.1 y - 0.1 y^2 \quad (4.40b)$$

$$r_z = 0.1 y \quad (4.40c)$$

The complete attainable region is shown in Figure 4.7a, and the axis are defined as follows:

x - Blue	Range: 0 to 1
y - Red	Range: 0 to 0.5
z - Green	Range: 0 to 0.65

Plug flow trajectories are drawn in blue and C.S.T.R. loci in red. The planes forming the hull are drawn in black. The following method was used to find the attainable region.

Step 1:

The trajectory of the plug flow reactor from the feed (pure A) was found numerically and the convex hull of the trajectory determined. The hull of the plug flow trajectory is the fan hull, ie the plug flow trajectory is strictly convex. The rate vector points outwards on the feed fan, between the dotted line and the feed point, and on the equilibrium fan, between the dotted line and the plug flow trajectory, as shown in Figure 4.7b. The rate vector is nearly tangential to both surfaces in these regions.

Step 2:

As the rate vector was close to tangential near the plug flow trajectory, it was thought that C.S.T.R.'s with feed points on the trajectory would extend the region. C.S.T.R.'s from various feed points along the plug flow trajectory were thus included and the convex hull of these was found. The hull is expanded by the inclusion of two equilibrium points:

- the equilibrium point of the C.S.T.R. that produces the most D and
- the equilibrium point of the C.S.T.R. from the feed point (this equilibrium point is the origin).

Figure 4.7a: The Attainable Region For Denbigh Kinetics

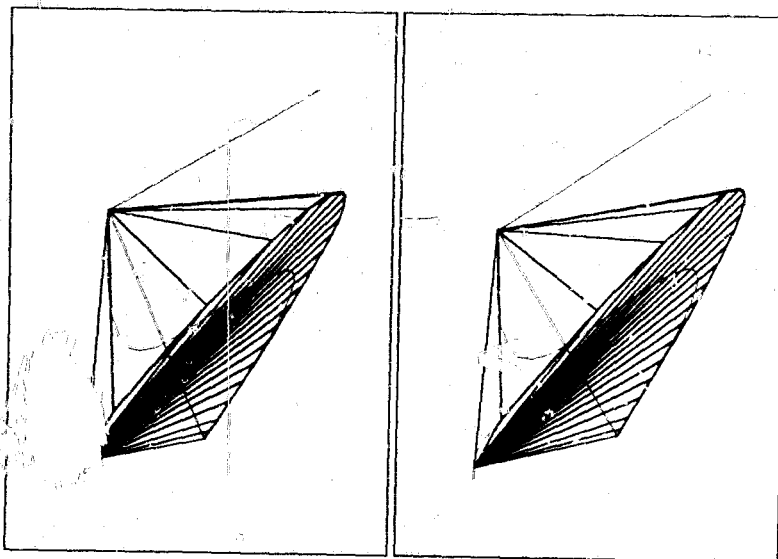
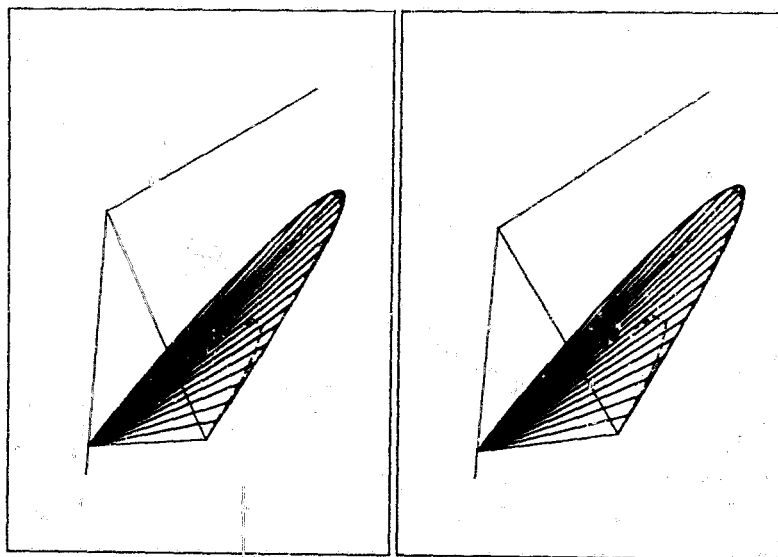


Figure 4.7b: The Convex Hull of the Plug Flow Trajectory



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It is found that no rate vectors point outwards on this hull.

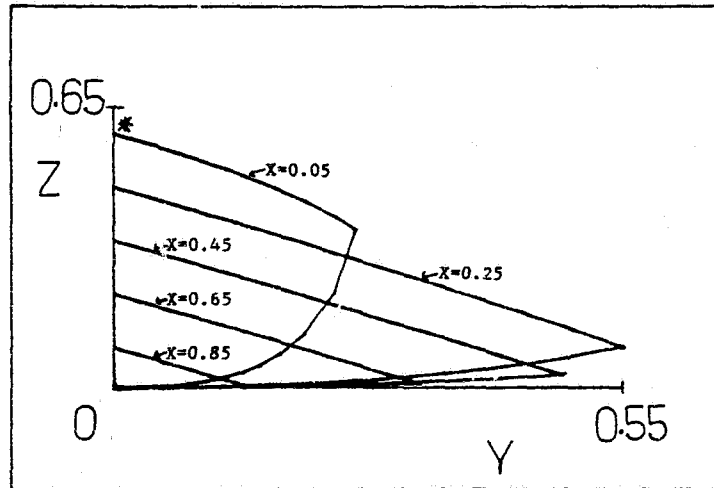
The attainable region is thus found to be made up of the origin, the plug flow trajectory from the feed point and a C.S.T.R. in series with this. The feed point of the C.S.T.R. must be that it gives the highest possible equilibrium concentration of D. (This is the point along the plug flow trajectory where the sum of the concentrations of B and D is the largest.) The hull is made up of two fans - one radiating from the origin to all the points along the plug flow trajectory and the other radiating from the C.S.T.R. equilibrium point to the plug flow trajectory. There is also a plane between the feed point and the two C.S.T.R. equilibrium points.

Once we have determined the hull we can then find the optimum reactor structure to give the highest concentration of D at a 95 % conversion of A. This can be done by plotting the contour curves of the attainable region (as shown in Figure 4.7c) and determining the optimal structure from the shape of the hull directly and then optimizing analytically. These ways will be discussed separately.

### Contour Plot

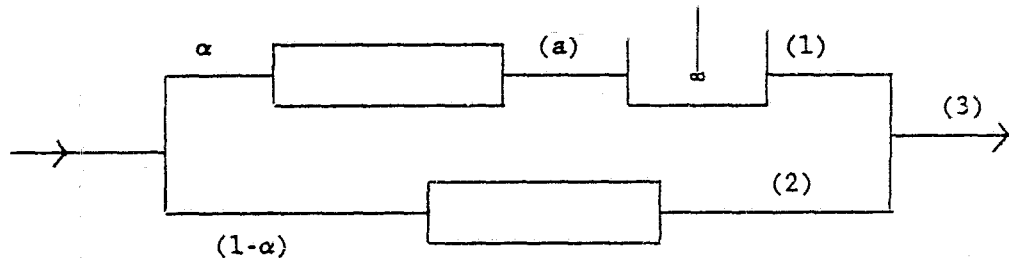
The contour plot (Figure 4.7c) shows slices of the hull for different values of  $x$ . The curves of the hull are thus made up of sections of the two fan structures. The point at the edge of the two curves is that of the plug flow trajectory. The maximum concentration of D is 3.53 mol/l (shown as point \*). This concentration would be achieved by mixing material from the top equilibrium point with feed.

Figure 4.7c: The Contour Plot of the Attainable Region



Analytical Optimization

The optimal operating point can be seen to be on the face formed by the fan from the top C.S.T.R. equilibrium point and the plug flow trajectory ie this can be interpreted as the following reactor structure:



The concentration at (a) must be such that the equilibrium concentration of D at (1) is as high as possible ie the point (a) corresponds to the point on the plug flow trajectory where the sum of the concentration of B and D is as high as possible.

The concentration at (2) and the ratio  $\alpha$  must be chosen to give a conversion of 95% and the highest possible concentration of D. This optimization can be done using standard techniques.

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The following is found to be optimal:

	(a)	(1)	(2)	(3)
Concentration A	0.80432	0	6	0.3
Concentration B	2.53413	0	0	0
Concentration D	1.19273	3.72689	0	3.540522
Residence time	0.77 s	$\infty$	0	$\infty$

All concentrations are in mol/l. The ratio  $\alpha$  is found to be 0.95.

In summary, the optimal reactor structure is a plug flow reactor in series with a C.S.T.R. such as to produce the maximum concentration of D. Feed must be bypassed and mixed with the equilibrium material to give a 95 % conversion of A.

It can be seen that both the maximum concentration of D is much higher than and that the optimal structure is different from that found by Chitra and Govind. It is thought that there is an error in the results of Chitra and Govind as we are unable to reproduce their results for the residence times given.

### 4.8 Examples in Concentration-Time Space

By time, we refer to space time, which is defined in equation (2.3), and which is proportional to the volume of the reactor. This will enable one to answer questions such as: how does one make material of a certain concentration from a specified feed in the smallest volume of reactor. An interesting feature of the kinetics in this space is that the reaction vector is degenerate as it is constant in time domain. This will lead to some rather interesting results, specifically, that it is not common for the plug flow trajectory to be strictly convex, with the result that the convex hull of the trajectory has other types of faces and not only the fan hull found up to now.



4.8.1 Example 13: Van de Vusse Kinetics

In this example the attainable region was constructed in  $x$ - $y$ - $\tau$  space (where  $\tau$  is space time). The kinetics and variables are defined in Section 4.7.1. We constructed the region for a feed of  $x=1, y=\tau=0$  and kinetics of  $a_1=10$  and  $a_2=1$ . (The hull is easier to view with a smaller value of  $a_1$ , and thus a value of 10 is used.)

The complete attainable region is shown in Figure 4.8a, and the axis are defined as follows:

$x$ - blue	Range 0 to 1
$y$ - red	Range 0 to 0.12
$\tau$ - green	Range 0 to 150

Plug flow trajectories are drawn in blue and C.S.T.R.'s in red. The planes and lines forming the faces of the attainable region are drawn in black. The method of constructing the attainable region will be outlined below.

Obviously, the range in space time is from 0 to  $\infty$ , but in drawing the attainable region, we cut off the space time axis at some suitably large  $\tau$ , where the structure of the region has become clear.

Step 1:

The plug flow trajectory from the feed point was drawn and the hull of this trajectory was constructed and is shown in Figure 4.8b.

Notice that the hull is not a fan hull, but also contains a complex surface between points on the trajectory. This agrees with the results of equation (4.1) where it is predicted that the fan structure will break down. Again it is very messy to do analytically but can be done numerically. In practice, only two points should be joined together and not a few joined to one

Figure 4.8a: Attainable Region for the Van de Vusse Kinetics in  $x-y-\tau$  Space

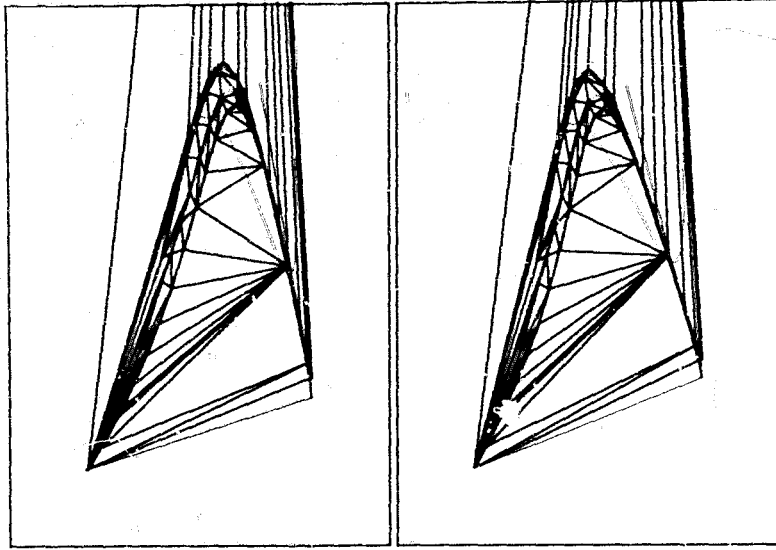


Figure 4.8b: Convex Hull of the feed plug flow trajectory

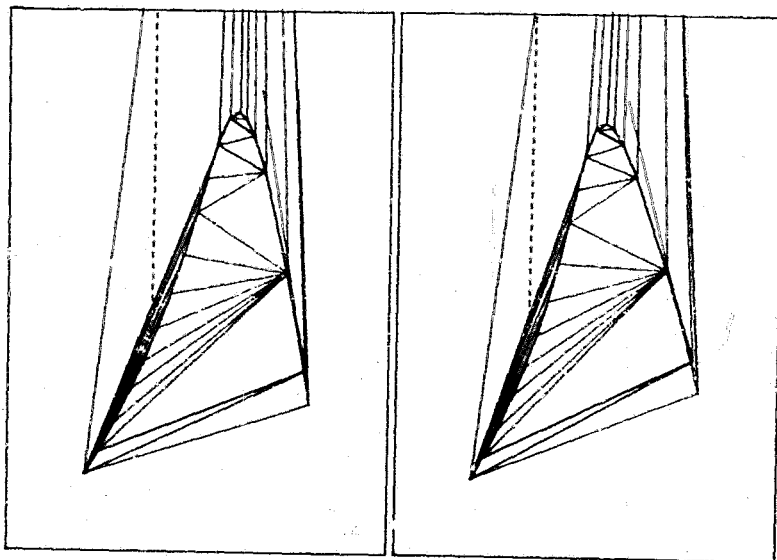
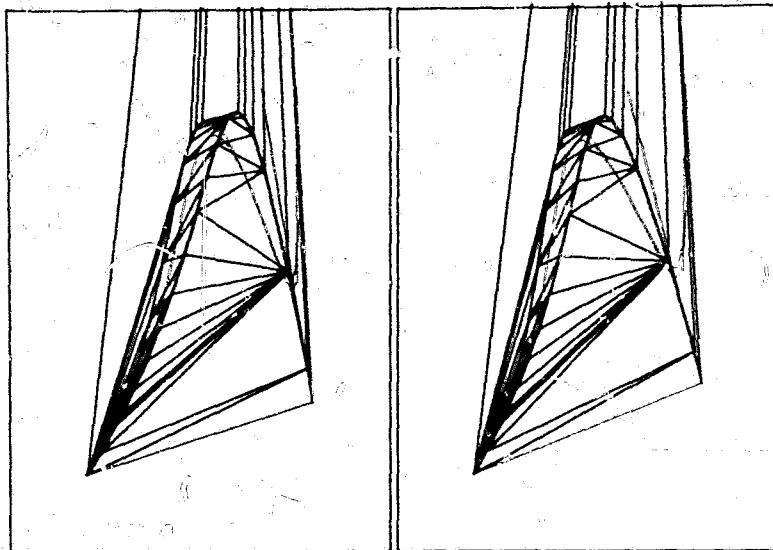


Figure 4.8c: Hull with the feed C.S.T.R. included



point as in the diagram. This is just numerical error, in that only a discrete number of points are used to construct the hull. The properties of the two points that are joined are that the reaction vectors and the line joining the points should be coplanar (see Section 4.3.2). Notice the plane between the feed point, the equilibrium point and a point on the plug flow trajectory. This large plane fills in the concavity in the plug flow trajectory in the projection in the x-y plane. This point will be characterized by the point where the reaction vector, the point, the feed point and the equilibrium point are all coplanar.

Note that the lines to the equilibrium point (ie as  $\tau \rightarrow \infty$ ) are all parallel. Thus any plug flow trajectory which starts on the line between the feed point and the equilibrium point will lie in the surface of the fan hull between the equilibrium point and the plug flow trajectory.

The reaction vector was found to point out of the hull from the feed point to the dotted line. Note that this line runs along the small section of feed fan and then along the plane (with x

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and  $y$  constant and varying  $\tau$ ). It is only a numerical problem that causes the line not to be parallel with the other lines to infinity.

### Step 2:

The next stage in the construction is to add the locus of the C.S.T.R. from the feed point and to construct the new hull. This hull is shown in Figure 4.8c.

It can be seen from the figure how the C.S.T.R. locus extends the region and how it forms part of the boundary of the region for part of the locus. The position of the plane has changed and the plane is now between the C.S.T.R., the feed point and the equilibrium point. Note that the C.S.T.R. and the plug flow trajectory both have the same equilibrium point.

The reaction vector was found to point out all over the surface formed between the plug flow trajectory and the C.S.T.R. locus.

### Step 3:

Plug flow trajectories from various points along the C.S.T.R. locus were drawn and the new convex hull constructed. This is shown in Figure 4.8a. Any plug flow trajectories with a feed point after the plane on the C.S.T.R. locus, lie inside the hull. The trajectory with a feed point on the vertex of the large plane formed by the feed point, the equilibrium point and a point on the C.S.T.R. locus extended the attainable region the most in the  $x$ - $y$  plane.

The other trajectories do not extend the hull in the  $x$ - $y$  plane but rather extend it in the time axis by forming a curved face between the plug flow trajectory from the feed point, and the one discussed above (ie the one which extends the hull the furthest in the  $x$ - $y$  plane).

As stated previously, the lines to infinity are parallel. Thus a plug flow starting from any point along the line between the

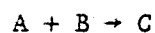
point that fills in the concavity on the C.S.T.R. locus and the equilibrium point will be the same trajectory, but displaced upwards on the time axis. These trajectories all project to the same trajectory in x-y space. Instead of drawing all the trajectories, only the first one is shown, and it must be remembered that the lines from the trajectory to the equilibrium point, represent a whole family of trajectories.

The boundary of the attainable region again only consists of plug flow trajectories and mixing lines. The C.S.T.R. locus which lies in the boundary of the attainable region forms bridging points to the plug flow trajectories.

When  $a_1 = a_2 = 1$ , the structure of the hull is rather different. In this case the projection of the plug flow trajectory to the x-y plane does not exhibit a concavity and thus the convex hull of the plug flow trajectory does not have the plane structure or section of feed fan, but rather has a fan structure along the whole plug flow trajectory. The reaction vector is tangential to this face. The other surface of the trajectory is similar to that discussed in the example, in that it is a complex structure between points on the plug flow trajectory, and no reaction vectors point out of this face.

#### 4.8.2 Example 14: Westerterp Kinetics

The following kinetics are known as the Westerterp kinetics:



Previous work on these kinetics is discussed in Section 1.4.5. All previous work looked at the problem of producing the most C in a given time from feed of pure A and pure B. This is unfortunately a four dimensional problem so we cannot look at it.

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The problem of producing the most C without a time constraint is rather uninteresting as a C.S.T.R. with equimolar feeds of A and B produces the most C. The attainable region is in this case a triangular pyramid with vertices at the origin, the points corresponding to pure A and pure B and the equilibrium point of the C.S.T.R. with equimolar feed.

One could rather try another interesting example based on these kinetics: for a given volume of reactor, how can one use up the most possible A and B. This requires a construction in A, B and time space. We will assume both the concentration of pure A and B to be equal and also that the rate constants for the two reactions are equal.

Define:

$$x = (\text{Concentration of A}) / (\text{Concentration of pure A (or B)})$$

$$y = (\text{Concentration of B}) / (\text{Concentration of pure A (or B)})$$

$$\tau = \text{space time}$$

The rates of reaction are:

$$r_x = -2x^2 - 2xy \quad (4.41a)$$

$$r_y = -2xy \quad (4.41b)$$

$$r_r = 1 \quad (4.41c)$$

The complete attainable region is shown in Figure 4.9. The axes are defined as follows:

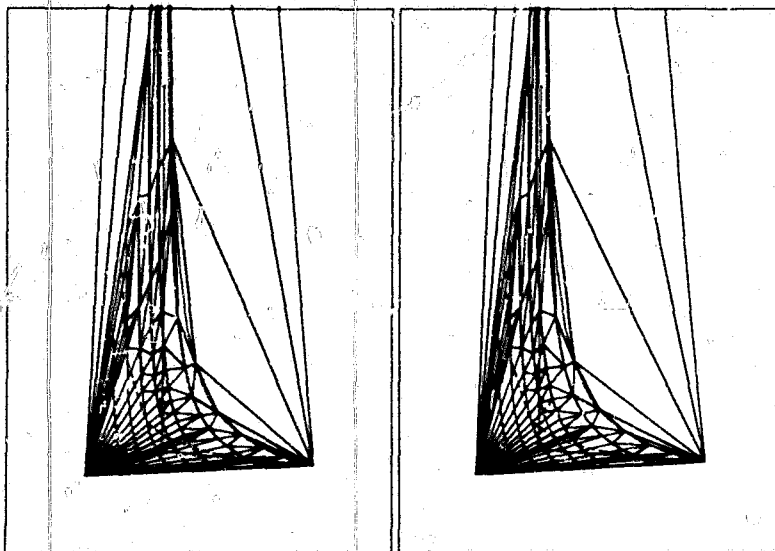
$$x = x = \text{blue} \quad \text{Range} = 0 \text{ to } 1$$

$$y = y = \text{red} \quad \text{Range} = 0 \text{ to } 1$$

$$z = \tau = \text{green} \quad \text{Range} = 0 \text{ to } 7$$

Plug flow trajectories are drawn in blue.

Figure 4.9: The Attainable Region for Westerterp Kinetics in A-B-r Space



Plug flow trajectories for various feed concentrations along the line joining pure A and B were drawn and the convex hull of these constructed. The plug flows lie inside the hull for part of the trajectory and then form part of the boundary after the dotted line as shown in Figure 4.9. The hull below the dotted line is a fan hull with the fan radiating from the point  $C^*$  representing pure B.

The dotted line represents the curve where the plug flow trajectories from the feed line move into the boundary of the attainable region. Mathematically this is described by the point along the plug flow trajectory where the reaction vector  $R$ , the line forming the hull  $(C^*-C)$  and the change in the reaction vector along this line  $(C^*-C)VR$  are coplanar. This is the situation discussed in Section 4.6, when the properties of the boundary of the attainable region were examined, and the dotted line is described by equation (4.14), with the proviso that  $C$  is a point on a plug flow trajectory with feed point on the line joining pure A and pure B, and  $C^*$  is the point from where the

fan structure originates, that is pure B. No reaction vectors point out of this region of the hull and so we have found the attainable region.

Note that there is no region in the space where the four vectors  $R_V$ ,  $VVR$  and  $RVR$  are coplanar. Thus a differential reactor does not lie in the boundary of the region.

#### 4.9 Examples in Concentration-Temperature Space

Temperature is an interesting variable, in that the rate of change of temperature is just a linear combination of the rates of reaction of the reactants (assuming the enthalpies of reaction to be constant). We thus might expect that this type of degeneracy in the kinetics would make it possible for the differential reactor to lie in the boundary of the attainable region. We will examine what happens in this case by means of an example.

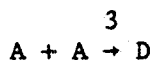
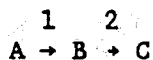
##### 4.9.1 Example 15: Non-Isothermal Van de Vusse Kinetics

In this example we consider the non-isothermal van de Vusse reaction. This example was considered by Chitra and Govind (1985b).



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The reaction scheme is as follows:



The numbers refer to the numbering of the reactions and not the order of reaction. Case 1 kinetics were used. The  $\Delta H$  of reactions used were different from those used by Chitra and Govind so as to make the problem three dimensional. The assumption used is that:

$$2 (\Delta H_{\text{rxn } 1} + \Delta H_{\text{rxn } 2}) = \Delta H_{\text{rxn } 3} \quad (4.32)$$

The same values of  $\alpha_1$  and  $\alpha_2$  were used and  $\alpha_3$  was modified accordingly. Because of this assumption, the results of Chitra and Govind cannot be compared with these.

The variables were defined as:

- T = Temperature / reference temperature
- x = Concentration A / reference concentration
- y = Concentration B / reference concentration

The reference concentration is pure A and the reference temperature is 300 K. The reaction rates are:

$$r_x = -k_1 x - k_3 x^2 \quad (4.33a)$$

$$r_y = k_1 x - k_2 y \quad (4.33b)$$

$$r_T = (\alpha_1 + \alpha_2) r_x + \alpha_2 r_y = -0.64 r_x - 0.28 r_y \quad (4.33c)$$

where:

$$k_1 = 5.4 \times 10^9 \exp \left[ \frac{-15840}{1.987 \cdot 300 \cdot T} \right] \quad (4.33d)$$

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$$k_2 = 1.6 \times 10^{12} \exp \left[ \frac{-23\,760}{1.987 \cdot 300 \cdot T} \right] \quad (4.33e)$$

$$k_3 = 3.6 \times 10^5 \exp \left[ \frac{-7\,920}{1.987 \cdot 300 \cdot T} \right] \quad (4.34f)$$

The reference concentration was taken as the feed concentration which was assumed to be pure A. The inlet feed temperature was varied from 200 to 650 K. This temperature range was used as it was found that all the interesting features of the hull occurred in this range.

Note that once the feed temperature to a reactor is fixed, the motion of the reactor is confined to a plane. Thus a plug flow trajectory and C.S.T.R. locus from the same feed point (and in fact any constant enthalpy reactor) will lie in the same plane. Furthermore, as the enthalpies of reaction are assumed to be constant in this example, the planes that the adiabatic reactors are confined to are all parallel.

The plug flow trajectories and the C.S.T.R. loci had to be determined numerically in this example. Thus it is difficult to determine the exact points where tangent planes touch the family of reactors and where reaction vectors point outwards etc. This may cause inaccuracies in the construction, but it is thought that the type of reactor structures that lie in the boundary of the region are correct. Thus the final optimization of the reactor structure, would be done separately as was done in Section 4.7.3, Example 12 for the Denbigh kinetics.

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The complete attainable region is shown in Figure 4.10a. The axis are defined as follows:

x - blue	Range - 0 to 1
y - red	Range - 0 to 0.8
T - green	Range - 200 to 750

Plug flow trajectories are shown in blue and C.S.T.R.'s in red. The construction of the attainable region is discussed below.

Step 1:

Plug flow trajectories from various points along the feed line (ie pure A and varying inlet temperature) are shown in Figure 4.10b. The dotted line is described by equation (4.14), with the proviso that  $Q$  are solutions to the plug flow trajectories with feed points on the feed line.

Figure 4.10a: The Attainable Region for Van de Vusse Kinetics in x-y-Temperature Space

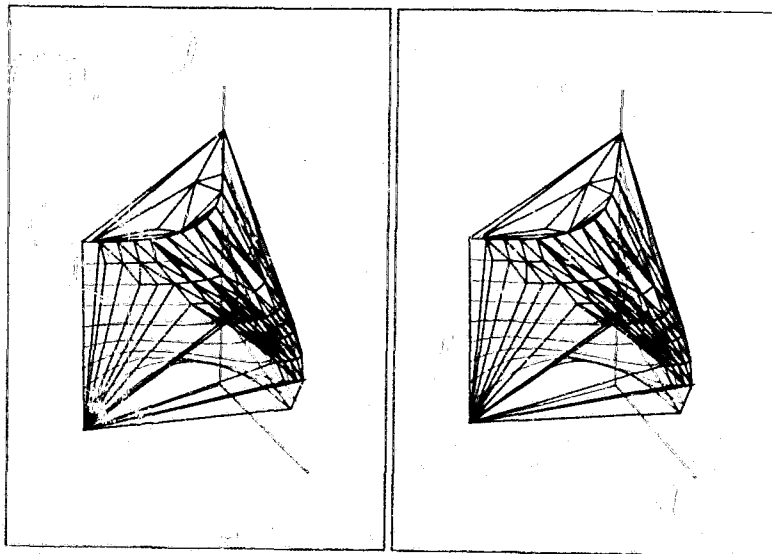


Figure 4.10b: Convex Hull of the plug flow trajectories

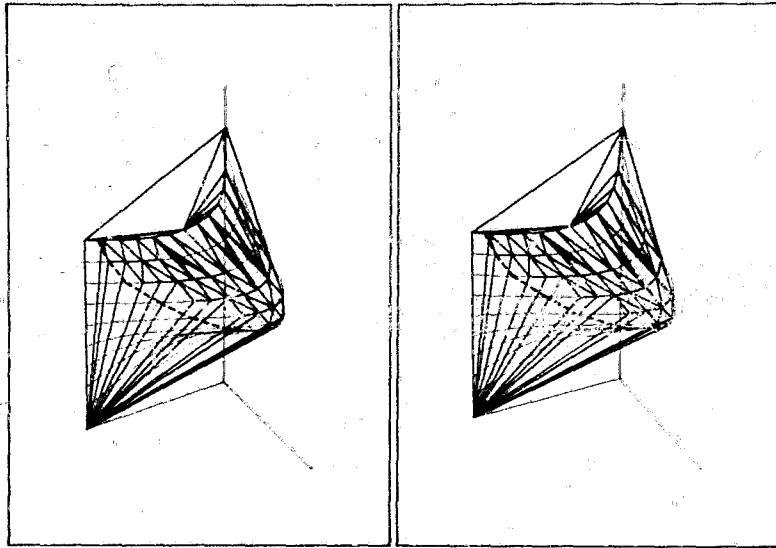
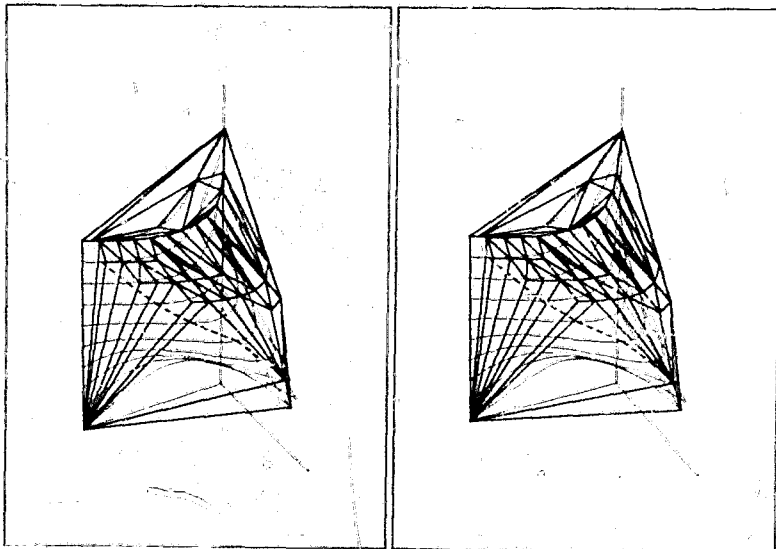


Figure 4.10c: Convex Hull with the C.S.T.R.'s included



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The reaction vector points out of the fan hull along the bottom of the hull, that is along the lines of the fan to the last plug flow trajectory.

Step 2:

C.S.T.R.'s from various point along the feed line were then added and the new convex hull is shown in Figure 4.10c. The C.S.T.R. loci lie inside the plug flow trajectories at the higher temperatures, but at the lower temperatures they extend the hull. It is interesting to note how they extend the hull in this example. The C.S.T.R.'s with the colder feeds form a plane with the feed point and a plug flow trajectory with an intermediate feed temperature. Thus in this case the tangent plane to the family of C.S.T.R.'s lies inside the hull of the region. It would appear that the family of C.S.T.R.'s lies very close to the surface of the region.

The dotted line is where the family of C.S.T.R. loci satisfy equation (4.14). Note that this line lies inside the hull at the higher temperature and eventually touches the surface of the hull at lower temperatures. The dotted line also lies very close to the surface of the region. Reaction vectors point out of the curved surface formed by the C.S.T.R. loci. This occurs close to the dotted line.

Step 3:

Plug flow trajectories with feed points where the reaction vector points out of the hull, were included in the hull. This completed the hull.

Note that at a feed temperature of about 450 K, the C.S.T.R. and plug flow trajectory touch, and the plug flow trajectory from the C.S.T.R. locus and that from the feed point corresponds. This is the point where the curves formed by the plug flow trajectories satisfying equation (4.14) and that by the C.S.T.R. loci satisfying the equation, intersect. At higher temperatures the

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C.S.T.R.'s lie inside the hull and at lower temperatures, the C.S.T.R. extend the hull. Notice however, that a differential reactor does not lie in the boundary of the hull. One might ask if the feed points to the plug flow trajectories that form the curved surface of the hull, could be achieved by a differential reactor, such as the maximum mixedness reactor.

In this space, the three vectors  $\underline{R}$ ,  $\underline{V}$  and  $\underline{VVR}$  are coplanar when either:

$$V_T + 0.64 V_x + 0.28 V_y = 0 \quad (4.35a)$$

$$\text{or } r_x (\underline{VVR})_y - r_y (\underline{VVR})_x = 0 \quad (4.35b)$$

where  $(\underline{VVR})_i$  is the  $i$ th component of vector  $\underline{VVR}$ . If the first equation holds, then the fourth vector  $\underline{RVR}$  is also in the plane and thus all four vectors are coplanar which is the necessary condition for a differential reactor to lie in the boundary of the attainable region. However the first equation also defines the plane to which a constant enthalpy reactor, with the mixing point as the feed point, is confined to lie. We know from our examples in two dimensions, that a differential reactor would neither lie in the boundary or extend the attainable region in this two dimensional space.

If the second equation holds over a region in the space, then the fourth vector  $\underline{RVR}$  would not generally lie in the plane of the other three vectors and it would depend on the kinetics whether this were possible or not. The only special condition under which the four vectors would be coplanar over a region in space would be if the reaction vector and the mixing vector were collinear along the region (ie a C.S.T.R. solution). This would again happen only for the C.S.T.R. where the mixing temperature and the feed temperature coincided. As discussed above, in this case the differential reactor would not extend the region.

## 4.10 Examples in Concentration-Time-Temperature Space

This space offers the most degeneracy of all the general three dimensional spaces. If  $r_x$  is the rate of formation of the species, and  $T_{ad}$  is the adiabatic temperature rise associated with the reaction, then the reaction vector  $\underline{R}$ , in Temperature(T)- Concentration(x)-Space Time( $\tau$ ) space, will be:

$$\underline{R} = (T_{ad} r_x, r_x, 1) \quad (4.36)$$

The three vectors  $\underline{R}$ ,  $\underline{V}$  and  $\underline{VVR}$  will be coplanar when  $V_T = T_{ad} V_x$ . When this is true, then the fourth vector  $\underline{RVR}$  will also be coplanar. However, the condition confines the reactor to lie in the constant enthalpy plane with the feed temperature equal to the mixing temperature. Again, we know for a region confined to a two dimensional plane, only plug flow trajectories or C.S.T.R.'s will form the boundary of the region.

The other case when the three vectors will be coplanar is when:

$$\frac{\partial r_x}{\partial x} V_x + \frac{\partial r_x}{\partial T} V_T = 0 \quad (4.37)$$

In general  $\underline{RVR}$  will not be coplanar with the other three vectors at points where the above equation is satisfied and which do not satisfy the C.S.T.R. equation. Thus in this extremely degenerate space, the differential reactor will not, in general, lie in the boundary of the attainable region.

Thus, rather than construct the unconstrained attainable region, we will show how a constrained attainable region can be constructed in three dimensional space.

## 4.10.1 Example 16: Cold Shot Cooling

In this example we consider the problem of cold shot cooling ie a system of adiabatic plug flow reactors with bypassing of the feed to cool the outlet stream from one reactor before it enters the next reactor. The optimization of this system of reactors consists of finding the optimal positioning and quantity of the cold shot cooling, the space times of the plug flow reactors and the feed temperature to the first reactor (and therefore of the cold shot) in order to get a specified outlet concentration.

This problem was examined previously in two dimensional concentration-time space in Section 3.3.3. We will be considering the same kinetics again.

The rate of formation is defined as:

$$r_x = 5E5 \exp(-4000/T)*x - 5E8 \exp(-8000/T)*(1-x) \quad (4.38)$$

where  $x$  is concentration and  $T$  is temperature. The temperature for an adiabatic constant pressure process with constant specific heat and heat of reaction is given by:

$$T = T^* + T_{ad} (1-x) \quad (4.38a)$$

where  $T^*$  is the feed (ie at a concentration of 1) temperature and  $T_{ad}$  is -200.

Notice that the reaction vector is only dependent on two of the parameters, namely concentration and temperature, and has a constant component in the time-axis domain.

The plug flow trajectories are drawn in blue and the faces of the hull is drawn in black.

The axis are as follows:

Temperature =	blue	Range 250 to 500
Concentration =	red	Range 0 to 1
Time =	green	Range 0 to 4



The following construction method was used:

Step 1:

Plug flow trajectories for a feed concentration of 1, space time of 0 and inlet temperatures  $T^*$  between 250 and 350 were drawn and the hull constructed.

The convex hull is a complex structure. Again the fan structure is found and the end points of this structure are defined by equation (4.14). The mixing point corresponds to feed material at the lowest temperature and the other point of  $\underline{V}$  lies on a plug flow trajectory. Equilibrium is represented by a line at  $t \rightarrow \infty$  with varying concentrations and temperature. Instead of considering the trajectories to infinity in this construction, we arbitrarily integrated the trajectories to a time of 4 where the trajectories were nearly vertical lines. The upper surface of the hull is not too important for the optimization problem as one would normally be interested in the minimum time required for a specified concentration. The structure of the hull, if the equilibrium points are included, can be visualized as all the faces connected to the equilibrium points would become vertical.

The hull shown in Figure 4.11a is thus the attainable region for a family of adiabatic plug flow reactors with bypass. The optimal operating conditions for an adiabatic plug flow reactor (optimal in that the time is a minimum for a given outlet concentration) can not be clearly seen from this view. The optimal operating point for a specified concentration would be the point where a vertical plane at the specified concentration intersected the hull at the lowest time. The curve formed by the fan hull and which is clearly shown in this view, represents the optimal position to mix the cold shot with. As shown in the previous discussion in two dimensions, these two curves are not the same. However as the cold shot temperature is lowered, the curves move closer and closer, until for an infinitely low temperature, which is equivalent to interstage cooling, the two curves correspond. This is easily visualized, as if the mixing point for the fan is moved further and further to the left, the fan lines will become more nearly parallel; until they eventually

Figure 4.11a: Attainable Region for a 1 Stage Cold Shot Cooled Reactor

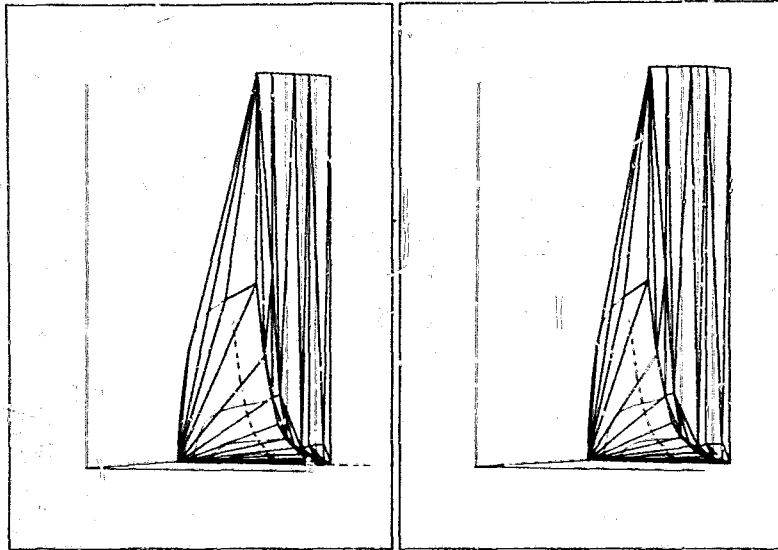
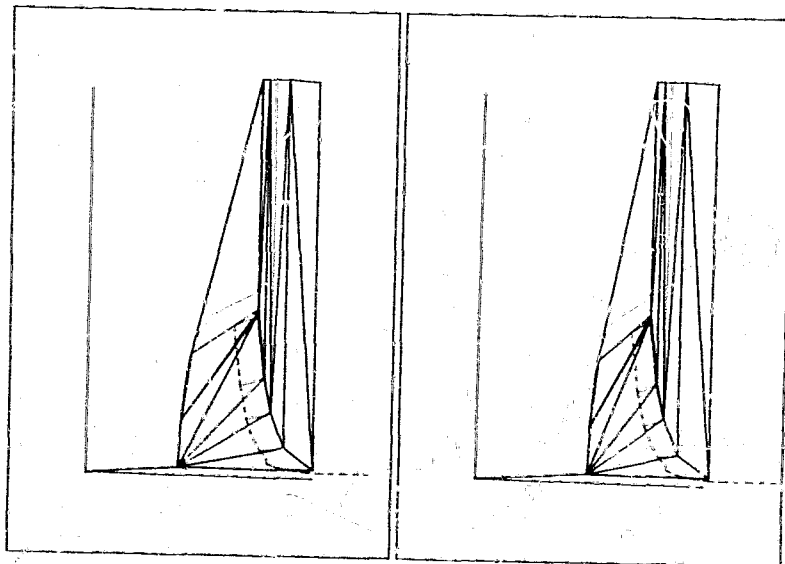


Figure 4.11b: Attainable Region for a 2 Stage Cold Shot Cooling Reactor



correspond to the line representing the lowest possible time for a specified concentration. This again agrees with our previous results for interstage cooling (Section 3.3.2).

The reaction vector points outwards between the dotted line and the curve described above. Thus a second stage of plug flow reactors will extend the hull.

Step 2:

We next draw the plug flow trajectories with feed points on the dotted line.

The plug flow trajectories that start on this line (ie where the reaction vector is tangential to the fan face) form the new boundary of the attainable region for a two stage cold shot cooling reactor. Again the curve that represents the maximum outlet concentration for the lowest space time for a two stage process cannot be clearly seen in this view. The curve that the edges of the second stage reactors make is the optimal operating points for bypass for the next stage. Comparing this figure to the previous one shows how the attainable region has been extended.

The attainable region for an n-stage cold shot cooling reactor with a range of possible feed temperatures could thus easily be constructed by adding plug flow trajectories and then making the hull. The relationship between the interstage cooling and the cold shot cooling problems is also easily visualized. It can also be seen how constrained optimization problems can be handled in three dimensional examples.

## 4.11 Discussion

It has been shown that the attainable region can be constructed for three dimensional examples with specified kinetics for both unconstrained and constrained reactor structures. The construction can be done relatively quickly and easily, in fact it can be done on an IBM compatible PC.

From the examples given, it would seem that only plug flow trajectories and C.S.T.R.'s lie in the boundary of the attainable region. Furthermore, it would seem that for an unconstrained attainable region, usually only the feed C.S.T.R. lies in the boundary of the region. Other C.S.T.R.'s at most touch the boundary at a point. It would also seem that it is not usual for a family of C.S.T.R.'s to touch the boundary of the region. Let us examine why this is.

Firstly, for a family of C.S.T.R.'s to lie in the boundary of the attainable region, the curve  $\Phi$  where the family touches the boundary would be described by equation (4.14) ie:

$$S = \underline{VVR} \cdot (\underline{VxR}(C)) = 0 \quad (4.14)$$

This equation describes the condition under which the family of plug flow trajectories with feed points on the curve  $\Phi$  would be tangential to the surface formed by the fan structure containing  $\underline{V}$ . However, for the family of C.S.T.R.'s to lie in the boundary of the region along  $\Phi$  implies that the fan structure containing the vector  $\underline{V}$  is tangential to the C.S.T.R.'s along  $\Phi$  as well.

This would occur firstly when the tangent to a C.S.T.R. at point  $C$ ,  $\underline{T}(C)$  also lay in the plane of  $\underline{V}$  and  $\underline{R}(C)$ , and secondly if the change in the tangent, ie the derivatives of the tangent vector, lay in this plane as well. Thus:

- (i)  $\underline{T}(C)$  would be in the plane of  $\underline{R}(C)$  and  $\underline{V}$ , ie  $\underline{T}(C) = \alpha \underline{R} + \beta \underline{V}$ ;
- (ii)  $\underline{VVR}$  would be in the plane of  $\underline{R}$  and  $\underline{V}$ ;
- (iii) If the derivatives to the tangent  $\underline{T}$  of the C.S.T.R. were to lie in the plane as well, this would presumably mean that as

$\underline{T}$  at the point is in the plane of  $\underline{R}$  and  $\underline{V}$ , that both  $\underline{VVR}$  and  $\underline{RVR}$  would also lie in the plane of  $\underline{R}$  and  $\underline{V}$ .

Thus it would seem that the stringent restriction that  $\underline{V}$ ,  $\underline{R}$ ,  $\underline{T}$ ,  $\underline{VVR}$  and  $\underline{RVR}$  are all coplanar must be met in order for a family of C.S.T.R.'s to touch the boundary of the attainable region.

RESULT 43

Now in order for the reaction vector to be tangent to the surface, the mixing vector of the C.S.T.R. would need to lie in the boundary of the region. This could only happen if the feed point to the C.S.T.R. and the vector  $\underline{V}$  along the fan structure were coplanar. In other words, the fan structure which contains  $\underline{V}$  and  $\underline{T}$  must in this case degenerate to a plane - ie it cannot be curved. Thus the boundary of the attainable region which contained the C.S.T.R.'s would be planar, and would contain the feed points of all the C.S.T.R.'s, the mixing point of the degenerate fan structure as well as the curve  $\Phi$ .

RESULT 44

These conditions seem very similar to those derived for a differential reactor that lies in the boundary of the attainable region. To recap on these conditions, in order for a differential reactor to lie in the boundary of the region, the four vectors  $\underline{V}$ ,  $\underline{R}$ ,  $\underline{VVR}$  and  $\underline{RVR}$  would have to be coplanar (from Result 39). Consider what this implies. The differential reactor locus is described by:

$$\frac{dC}{dr} = q\underline{V} + \underline{R} \quad (4.8)$$

The curvature of a differential locus, when all four the vectors mentioned above are coplanar, is from equation (4.13) zero; implying that the differential reactor that lies in the boundary of the region must move in a plane that contains the mixing point. The reaction vectors must be tangential to this plane and thus point backwards along the plane. The point along the edge of the plane where the reaction vector, when projected backwards, intersects would be a feed point for a C.S.T.R. that could be used to achieve the point along the differential reactor locus. Thus it would seem that the differential reactor need not be

considered, as any place where it lay in the boundary could be reached by a family of C.S.T.R.'s as well.

RESULT 45

The conditions for a family of C.S.T.R.'s to lie in the boundary of the attainable region are extremely stringent in that there are many constraints on the reaction vector. It is more usual to find during a construction that the tangent plane to the family of C.S.T.R.'s does not lie in the surface described by equation (4.14). Usually the reaction vectors point outwards along the curve where the fan structure is tangential to the C.S.T.R.'s. In this case the reaction vector becomes tangent further back or closer to the mixing point of the fan as happened in Examples 10 and 15. Furthermore in these cases, the fan structure does not degenerate to a planar structure but remains a curved surface.

It has been demonstrated that both the constrained and unconstrained attainable region can be constructed. The question now arises: how accurate are the constructions of the attainable region given in the examples? The examples were constructed using a combination of numerical calculations and analytical conditions. It is therefore difficult to determine if the regions are exactly correct. However I am fairly certain that the reaction vectors along the proposed attainable regions, if not exactly tangent, do not point out by too much. This would imply that if the reaction vector does point out over a section of the region, the addition of reactors will not extend the region by too much for the given kinetics.

This might be felt not to be all that satisfactory, and perhaps by writing sophisticated computer programs to solve the tangency conditions and the various equations that were found to describe the surface of the region, one could improve the accuracy. This was not done by the author. The author in fact made a policy of keeping the computer programs as simple as possible so that firstly, the programs could be continuously modified to incorporate new ideas, and secondly, the emphasis was on the properties of the attainable region and not just the mechanics of constructing the region. All the programming was interactive, in that the types of reactors and the feed points to them were decided by the author at each stage. All the computations were done on a basic model IBM compatible PC.

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The reasoning given in this chapter is rather geometrical and has been discussed in terms of the properties of the different types of reactors and the surface of the region. In the next section, the properties of a general  $n$ -dimensional attainable region will be developed rather more rigorously.

CHAPTER 5

EXTENSIONS TO HIGHER DIMENSIONS AND CONCLUSIONS

5.1 Introduction

Many interesting examples where there are more than three independent variables have not as yet been handled. These problems would require the construction of the attainable region in higher dimensions. Many of the properties of the attainable region that were previously derived will hold in higher dimensions. However, as the structures making up the faces of the hull increase in complexity as the dimension of the hull increases, this could perhaps introduce further results. Routines to determine the convex hull of a set of points in any dimensional space do exist, and at present finding more efficient routines is a fairly active field of research. No reference to work on properties of convex hulls in vector fields or even much that is useful for this particular application of convex hulls of functions has been found. This too appears to still be a very new and active field in mathematics.

The problem of finding the attainable region in higher dimensions has not been solved and there are still many unanswered questions. In this chapter the results that do apply to any dimensional space will be stated and thereafter further properties will be speculated upon. In this chapter it will always be assumed that we are working in an  $n$ -dimensional space and that the variables of this space are not linearly dependent. This implies that we will not be working in a  $(n-1)$  or lower dimensional subspace of the  $n$ -space.



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