

A BIFURCATION PROBLEM  
ARISING FROM  
CHEMICAL ENGINEERING.

Neil Coghlan      14th. December 1986

## ACKNOWLEDGEMENTS

For their assistance, encouragement, and continuing support over the last two years, I wish without prejudice, to sincerely thank the following people

|                    |                               |
|--------------------|-------------------------------|
| Prof Alastair Wood | Head of Mathematical Sciences |
|--------------------|-------------------------------|

|                    |                   |
|--------------------|-------------------|
| Dr Emmanuel Buffet | My tutor - Year 2 |
|--------------------|-------------------|

|                   |                   |
|-------------------|-------------------|
| Dr David Reynolds | My tutor - Year 1 |
|-------------------|-------------------|

I also wish to thank Specialty Materials Ireland for facilitating my study leave, funding my course and specifically for their continuing policy in encouraging further education

A special word of thanks to my wife, for her full support, and for typing the text

To my son, Conor

## TABLE OF CONTENTS

|                                                     | PAGE |
|-----------------------------------------------------|------|
| CHAPTER I                                           |      |
| CHEMICAL REACTORS - DESIGN AND MODELLING            |      |
| 1 1 REACTION KINETICS AND REACTOR DESIGN            | 1    |
| 1 2 THE CONTINUOUS STIRRED TANK REACTOR             | 7    |
| 1.3 MIXING OF FLUIDS                                | 9    |
| 1 4 FIRST ORDER REACTIONS/OSCILLATORY BEHAVIOUR     | 11   |
| 1.5 FORMATION OF THE GOVERNING EQUATIONS            | 13   |
| CHAPTER II                                          |      |
| EXISTENCE, UNIQUENESS, AND BOUNDEDNESS OF SOLUTIONS |      |
| 2 1 EXISTENCE AND UNIQUENESS                        | 18   |
| CHAPTER III                                         |      |
| LOCAL PROPERTIES                                    |      |
| 3 1 EXISTENCE OF EQUILIBRIA                         | 25   |
| 3 2 MULTIPLICITY OF STEADY STATES                   | 27   |
| 3 3 STABILITY OF CRITICAL POINTS                    | 29   |
| 3 4 STEADY STATE RESPONSE                           | 32   |
| CHAPTER IV                                          |      |
| BIFURCATION PHENOMENA                               |      |
| 4 1 PERIODIC BIFURCATION THEORY                     | 34   |
| 4 2 STABILITY OF THE BIFURCATING ORBIT              | 40   |
| 4.3 DEVELOPMENT OF HOPF'S BIFURCATION THEORY        | 44   |
| 4 4 DIRECTION OF BIFURCATION                        | 48   |

## CHAPTER V

## NUMERICAL ANALYSIS

|     |                                                            |    |
|-----|------------------------------------------------------------|----|
| 5.1 | NUMERICAL ALGORITHMS GROUP - N A G                         | 56 |
| 5.2 | THE DO2-EBF DRIVER ROUTINE                                 | 59 |
| 5.3 | CLASSIFICATION OF DYNAMIC BEHAVIOUR IN<br>PARAMETRIC SPACE | 68 |
| 5.4 | SAMPLE PROGRAMME RESULTS                                   | 70 |
| 5.5 | ANALYSIS OF DATA                                           | 72 |
| 5.6 | DISCUSSION OF NUMERICAL RESULTS                            | 77 |

|  |                                 |    |
|--|---------------------------------|----|
|  | CONCLUSIONS AND RECOMMENDATIONS | 80 |
|--|---------------------------------|----|

## APPENDICES

|   |                                 |    |
|---|---------------------------------|----|
| A | MULTIPLICITY CONDITION          | 82 |
| B | DETERMINANT AND TRACE FUNCTIONS | 83 |
| C | ROOTS OF THE TRACE FUNCTION     | 85 |
| D | CHEMICAL REACTOR CONTROL THEORY | 86 |

|  |              |    |
|--|--------------|----|
|  | BIBLIOGRAPHY | 96 |
|--|--------------|----|

## CHAPTER ONE

### 1. CHEMICAL REACTORS - DESIGN AND MODELLING

#### 1.1 Reaction Kinetics and Reactor Design <sup>9)</sup>

The ultimate goal of a chemical engineer in dealing with chemical reactions generally includes:

- 1) Selection of the reactor type among many designs.
- 2) Determination of the required reactor size.
- 3) Specification of operating conditions -

To achieve this goal he/she must have knowledge of the rate of chemical reaction, the conversions obtainable, the nature of physical processes interacting with the chemical reaction, and the parameters which influence the preceding

The rates of physical processes e.g. mass transfer and heat transfer, can be adequately estimated in many cases from the properties of substances participating in the reaction, flow patterns, the geometry of the reaction vessel etc. On the other hand, chemical rate data for most industrially important reactions rely upon experimental investigation of the specific chemical reactions involved

#### Kinetics - Basic Terminology

The amount of a selected component A being converted per unit time per unit quantity of a reference variable  $y$  in a chemically reacting system is defined as the rate of reaction  $r_A$

$$r_A = \frac{1}{y} \frac{dN_A}{dt} \quad 1.1.1$$

Molal units are generally used as the amount  $N_A$  of the component being followed, the reference variable  $y$  in homogeneous fluid reactions is usually the volume of the reacting fluid  $V$  or of the reactor  $V_r$ .

In the case of the continuous stirred tank reactor the volume of the reacting fluid system remains constant, thus for a first order reaction,

$$r_A = \frac{dC_A}{dt} = -k C_A \quad (\text{moles/l.sec}) \quad 1.1.2$$

In this equation the proportionality constant  $k$  is termed the specific reaction rate or "the rate constant  $k$ " and it is markedly dependent upon temperature, through the Arrhenius equation

$$k = k_0 e^{-E/RT} \quad 1.1.3$$

Although this equation is about 80 years old, it predicts the effect of temperature on the rate constant, for simple reactions, so accurately that it still finds wide application in a great number of reaction kinetic problems.

In this equation  $E$  is the activation energy and was considered by Arrhenius as the amount of energy in excess of the average energy level which the reactants must have in order for the reaction to proceed.

In practice, most reactions important in industrial processes are quite complex in nature because their reaction mechanisms are considerably different from the stoichiometric equations. However, in dealing with reaction kinetics, one process may account for the major factor in determining the overall rate of reaction and is termed the "rate controlling step". My model for the C.S.T.R. will be based on some of the outlined fundamentals.

## Reactor Design

Since all chemical processes are centered around the chemical reactor, a most important factor in determining the over-all process economy is the reactor design.



2. Continuous Reactor. Reactants are introduced and products withdrawn simultaneously in a continuous manner in this type of reactor. It may assume the shape of a tank, a tubular structure, or a tower, and finds extensive applications in large-scale plants for the purpose of reducing the operating cost and facilitating control of product quality.

3. Semicontinuous Reactor In this category belong reactors that do not fit either of the above two types. In one case some of the reactants are charged at the beginning whereas the remaining are fed continuously as the reaction progresses. Another type is similar to a batch reactor except that one or more of the products is removed continuously.

Chemical reactors have also been basically classified according to their design features in four ways as represented diagrammatically in Fig. 1 1.1.

Fig 4 Main types of reactor

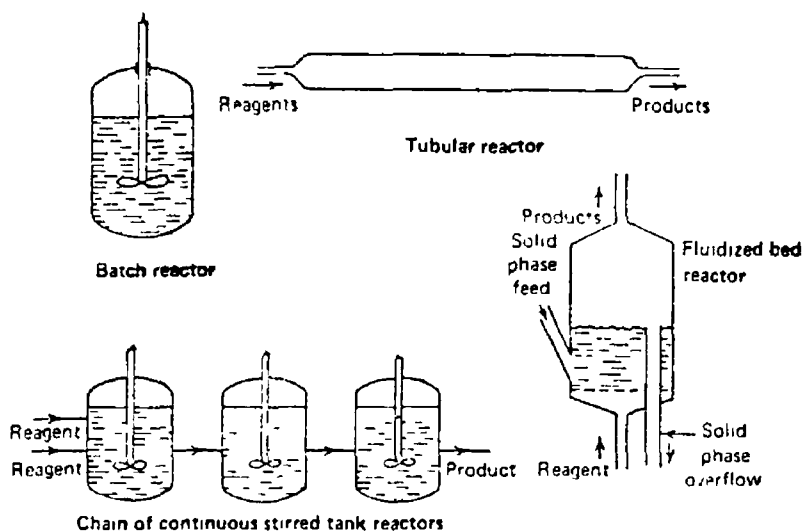


Fig. 1.1.1





### 3. Tower Reactor

A vertical cylindrical structure with a large height-to-diameter ratio characterises this type of reactor. It may have baffles or solid packing (reactant, catalyst, or inert) or may be simply an empty tower, and is employed in continuous processes involving heterogeneous reactions. Examples are the lime kiln, and gas-absorption units for gas-liquid reactions including packed towers, plate towers, and spray towers

### 4. Fluidized-bed Reactor.

This is a vertical cylindrical vessel containing fine solid particles that are either catalysts or reactants. The fluid reactant stream is introduced at the bottom of the reactor at a rate such that solids are floated in the fluid stream without being carried out of the system. Under this condition the entire bed of particles behave like a boiling liquid, which tends to equalize the composition of the reaction mixture and temperature throughout the bed (i.e, some degree of back mixture is obtained). This is generally considered one of the distinct advantages of the fluidized-bed reactor. The attrition of catalyst with entrainment of the resulting fines is one of the disadvantages. It has been applied extensively to solid-fluid reactions, such as the catalytic cracking of petroleum hydrocarbons, the conversion of uranium oxides to uranium fluorides, the reduction of some mineral ores, and the gasification of coal.

## 1.2 ABOUT THE CONTINUOUS STIRRED-TANK REACTOR (C.S.T.R.)

9)

This type of reactor consists of a well-stirred tank into which there is a continuous flow of reacting material, and from which the partially reacted material passes continuously. It is because such vessels are squat in shape (e.g. cylindrical vessels as wide as they are deep) that good stirring of their contents is essential; otherwise there could occur a bulk streaming of the fluid between inlet and outlet and much of the volume of the vessels would be essentially dead space.

The important characteristic of the C.S.T.R. is the stirring. The most appropriate first approximation to an estimation of its performance is based on the assumption that its contents are perfectly mixed. As a consequence the effluent stream has the same composition as the contents and this demonstrates the important distinction between the C.S.T.R. and the tubular reactor.

A fair approximation to perfect mixing is not difficult to attain in a C.S.T.R., provided that the fluid phase is not too viscous. In general terms, if an entering element of material, for example, a shot of dye is distributed uniformly throughout the tank in a time very much shorter than the average time of residence in the tank, then the tank can probably be taken to be 'well-mixed'. As shown overleaf in Fig. 1.2 1, several permutations are possible in the production assembly of a stirred tank reactor.

One great advantage of the C.S.T.R., apart from simplicity of construction, is the ease of temperature control. The reagents entering the first vessel plunge immediately into a large volume of partially reacted fluid and, because of the stirring, local hot spots do not tend to occur. Also the tanks of the C.S.T.R. offer the opportunity of providing a very large area of cooling surface. In addition to the external surface of the vessels themselves, a large amount of internal surface,

in the form of submerged cooling coils, can be provided. Sometimes, in place of coils, a calandria is used, as in the example of the Schmid nitrator for nitroglycerine. A further advantage, as compared to the tubular reactor, is the openness of the construction. This makes it easy to clean the internal surfaces and is important in the case of reactions where there is a tendency for solid matter to be deposited, e.g. polymerization processes and reactions in which tarry material is formed as a by-product.

For these various reasons the typical fields of application of the C.S.T.R. are continuous processes of sulphonation, nitration, and polymerization. It is used very extensively in the organic chemical industry and particularly in the production of plastics, explosives, and synthetic rubber. The C.S.T.R. is also used whenever there is a special necessity for stirring; for example, in order to maintain gas bubbles or solid particles in suspension in a liquid phase, or to maintain droplets of one liquid in suspension in another as in the nitration of benzene or toluene. The rate of such reactions can be very dependent on the degree of dispersion, and therefore on the vigour of agitation.

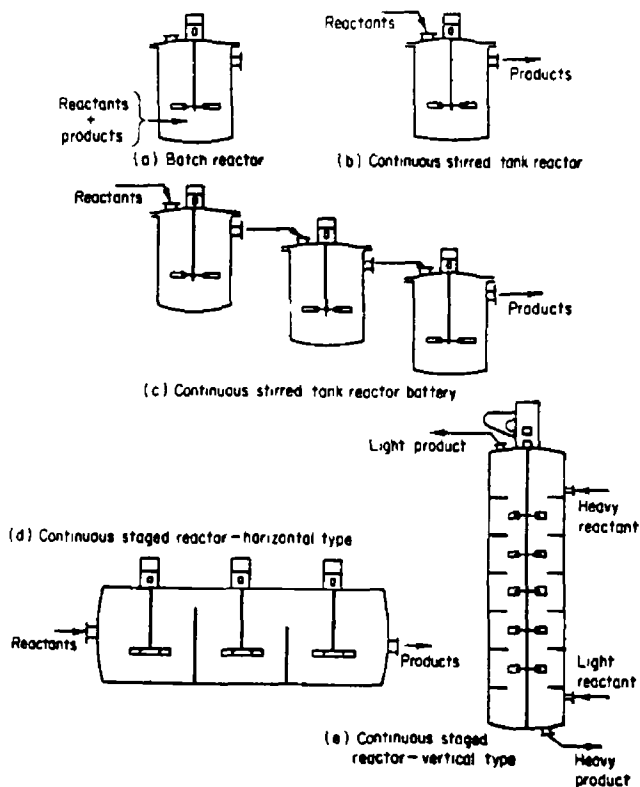
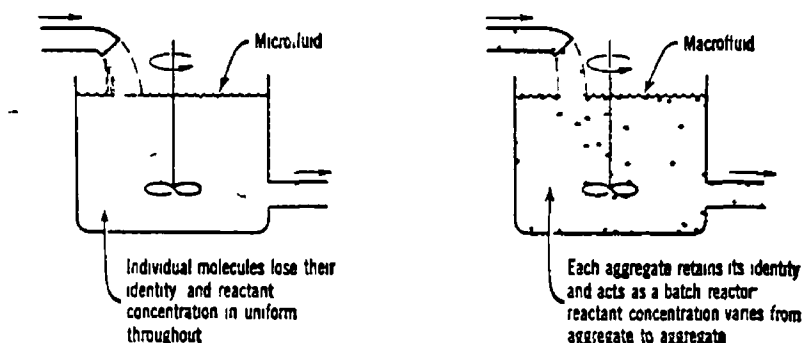


Fig. 1.2.1

The problem associated with the mixing of fluids during reaction is important for extremely fast reactions in homogeneous systems, as well as for all heterogeneous systems. This problem has two overlapping aspects: firstly the degree of segregation of the fluid, or whether mixing occurs on the microscopic level (mixing of individual molecules) or the macroscopic level (mixing of clumps, groups, or aggregates of molecules), and secondly the earliness of mixing, or whether fluid mixes early or late as it flows through the vessel.

First consider the degree of segregation of a fluid, and for convenience let us define terms to represent the extremes in segregation of a fluid. For this suppose that liquid A is available in two forms as shown below in Fig. 1.3.1. In the first form the liquid is as we normally imagine it, with individual molecules free to move about and collide and intermix with all other molecules of the liquid. One refers to such a liquid as a microfluid. In the second form liquid A is available in a large number of small sealed packets, each containing a large number, say about  $10^{12}$  to  $10^{18}$  of molecules. This type of liquid may be called a macrofluid.



Difference in behavior of microfluids and macrofluids

6)

Fig. 1.3.1

In the flow of an idealized microfluid and macrofluid tracer measurements cannot distinguish between them; however, for chemical reactions these fluids may behave quite different.

For a microfluid, individual molecules lose their identity and reactant concentration is uniform throughout. For a macrofluid, each aggregate retains its identity and acts as a batch reactor. Reactant concentration varies from aggregate to aggregate.

The normally accepted state of a liquid or gas is that of a microfluid, and discussions on homogeneous reactions are based on this assumption.

It will also be assumed that mixing and chemical conversion in the reaction vessel is instantaneous.

#### 1.4                    EXAMPLES OF FIRST ORDER REACTIONS AND OF OSCILLATORY BEHAVIOUR

The model to be subsequently studied is a first order irreversible exothermic non adiabatic reaction. The rate expression under constant volume conditions is given as

$$r_A = -k C_A \qquad 1.4.1$$

Typical examples of a first order reaction are

- 1] Thermal decomposition of  $H_2O_2$
- 2] Pyrolysis of ethane
- 3] Cyclotrimerization of butadiene over catalyst
- 4] Pyrolysis of Ca-oxalate
- 5] Gas-phase thermal decomposition of ditertiary butyl peroxide

A chemical system following different paths depending on whether a parameter is increasing or decreasing, is called chemical hysteresis. This model, under certain constraints, may give rise to hysteresis, oscillatory behaviour, and other interesting phenomena. Such behaviour has an electrical analog, a current-voltage curve resembling Fig. 1.4.1 in systems containing a negative resistance element. Magnetic hysteresis occurs in a ferromagnet on varying the direction strength of an applied magnetic field.

Quite a large number of reactions exhibiting multiple stationary states and chemical hysteresis have been investigated, especially by chemical engineers. One fairly simple example of such a system is the oxidation of thiosulphate by peroxide.

Figure 1.4.2 below illustrates some experimental results for this reaction, showing the steady-state temperature as a function of coolant flow rate.

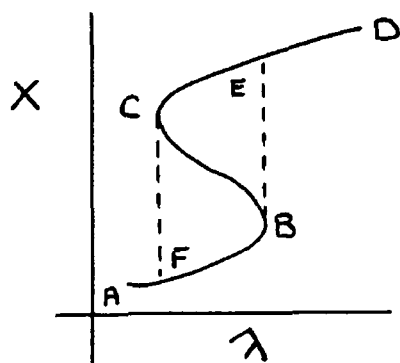


Fig 1.4.1

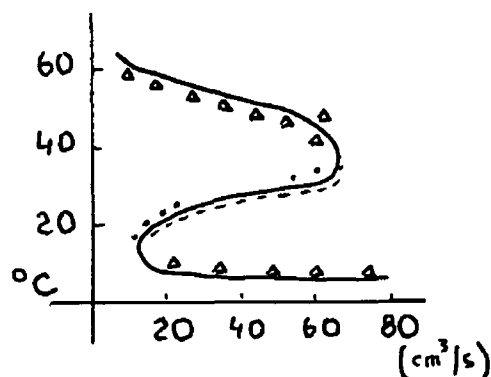


Fig. 1.4.2

We have seen how multiple stationary states can exist, and how a system can change from one set of such states to another when the external parameters are altered. But to obtain oscillatory behaviour like that of the heartbeat, one needs a mechanism that will switch the system back and forth without external intervention. One much-studied example of an oscillatory chemical reaction is the bromination of malonic acid in the presence of an oxidation-reduction couple, such as  $\text{Ce}^{\text{IV}}$ ,  $\text{Ce}^{\text{IV}}$  known as the Belousov-Zhabotinskii reaction.

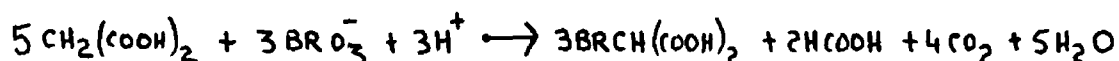


Figure 1.4.3 shows the oscillatory behaviour observed in this reaction. The oscillations persist in a well-stirred beaker for nearly an hour, as long as the concentration of reactants is such as to keep the system far from equilibrium; in an open system, fed with reactants and depleted of products, they can persist indefinitely.

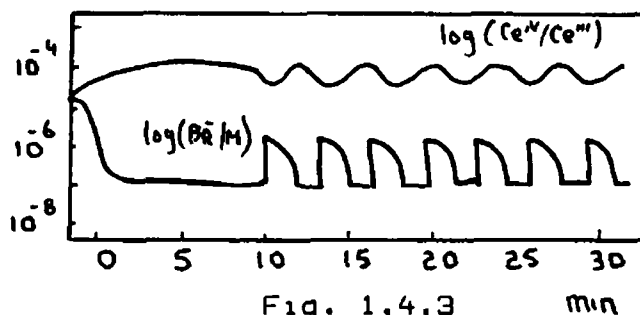


Fig. 1.4.3



## 1.5 FORMULATION OF THE GOVERNING EQUATIONS

Let us consider a continuous perfectly mixed stirred tank reactor with recycle. In order to define the problem more clearly the chemical reaction will be taken to be first order, exothermic non adiabatic, and irreversible. Thus



Furthermore, the following assumptions shall be made

1. Mixing is undelayed.
2. The chemicals behave as microfluids.
3. The heat capacity of the vessel and cooling coils may be ignored.
4. Thermal properties and inlet composition of the reactants are sensibly constant.
5. There is no feedback control.
6. Coolant temperature and recycle rates remain constant.

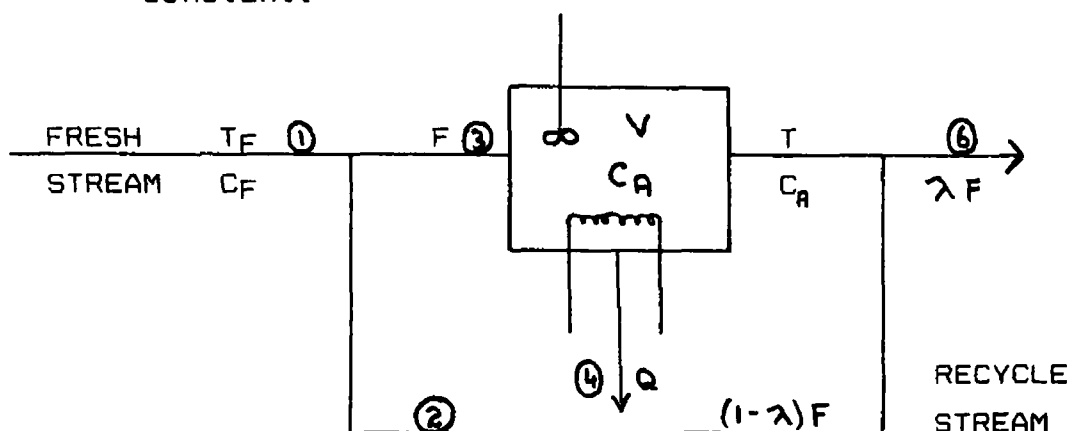


Fig. 1.5.1

A schematic picture of the C.S.T.R.

It will be shown that the concentration and temperature of A in the reactor may be modelled by a pair of coupled ordinary differential equations using material and enthalpy balances respectively.

# MATERIAL BALANCE ON REACTANT A

$$\sum \text{In} - \sum \text{Out} = \sum \text{Accumulation}$$

Apply the balance over a short time interval  $\Delta t$ . The entire flowrate to the reactor is  $F$  ( $\text{m}^3/\text{sec}$ ) including the recycle flowrate of  $(1-\lambda)F$ .

$$\begin{array}{ll} \text{In:} & 1 \quad \lambda F \cdot C_F \Delta t \\ & 2 \quad (1-\lambda) F C \Delta t \end{array}$$

$$\begin{array}{ll} \text{Out:} & 3 \quad F \cdot C \Delta t \\ & 4 \quad \tau \cdot V \Delta t \end{array}$$

$$\text{Accum:} \quad 5 \quad V \cdot C \Big|_{t+\Delta t} - V C \Big|_t$$

$$\text{Therefore} \quad V \frac{dc}{dt} = \lambda F (C_F - C) - V \tau \quad 1.5.2$$

$$\text{where } \tau = -k C \quad \dots \text{Rate of reaction}$$

$$\text{and } k = k_0 e^{-E/RT} \quad \dots \text{Arrhenius constant}$$

Introducing two dimensionless variables ( $x$ ,  $t$ ) and constants as follows help describe the system in the most economical way possible. 13)

$$x = \frac{C_F - C}{C_F} \quad \text{Dimensionless concentration}$$

$$\tau = \frac{V}{F \lambda} \quad \text{Reduced time} \quad 1.5.3$$

$$t = \frac{t'}{\tau} \quad \text{Dimensionless time}$$

Equation 1.5.2 now becomes,

$$\frac{dx}{dt} = -x + k \tau (1-x) \quad 1.5.4$$

However,  $k$  is temperature dependent through the Arrhenius function and further dimensionless parameters need be introduced as follows

$$\gamma = \frac{E}{RT_F} \quad \text{Arrhenius Constant}$$

$$\delta = k_0 e^{-\gamma} \tau \quad \text{Damkohler Constant} \quad 1.5.5$$

$$y = \left( \frac{T - T_F}{T_F} \right) \gamma \quad \text{Dimensionless Temperature}$$

However

$$\begin{aligned} \ln k &= \ln k_0 - \frac{E}{RT} \\ &= \ln k_0 - \frac{E}{RT_F} + \left( \frac{E}{RT_F} - \frac{E}{RT} \right) \\ &= \ln(\delta/\tau) + \frac{E}{RT_F} \left( 1 - \frac{T_F}{T} \right) \\ &= \ln(\delta/\tau) + \gamma \left( \frac{T - T_F}{T} \right) \\ &= \ln(\delta/\tau) + \left( \frac{y}{1 + y/\gamma} \right) \\ k \tau &= \delta \exp\left(\frac{y}{1 + y/\gamma}\right) \end{aligned} \quad 1.5.6$$

Thus, the material balance, as described by 1.5.4 now, finally evolves as a non-linear differential equation which is a function of two dimensionless variables ( $x$ ,  $y$ ) as follows:

$$\frac{dx}{dt} = -x + \delta(1-x) \exp\left(\frac{y}{1 + y/\gamma}\right) \quad 1.5.7$$

## ENTHALPY BALANCE ON REACTANT A

The heat balance is applied on reactant A over the open system as highlighted in Fig. 1 5.1.

Energy gained and lost in the inlet and outlet streams by heat transfer, accumulated within the vessel, and lost by both reaction and cooling, is designated, and indexed below relevant to the appropriate figure.

|                  |    |     |   |                                                |
|------------------|----|-----|---|------------------------------------------------|
| Bulk Transfer    | 1) | In  | I | $\lambda \rho F C_p T_F \Delta t$              |
|                  | 2) | In  | I | $(1-\lambda) \rho F C_p T_F \Delta t$          |
| Bulk Transfer    | 5) | Out | O | $\rho F C_p T \Delta t$                        |
| Loss by Reaction |    | Out | O | $\gamma V (-\Delta H) \Delta t$                |
| Loss by Cooling  | 4) | Out | O | $A A (T - T_c) \Delta t$                       |
| Accumulation     |    | Acc | A | $M C_p T \Big _{t+\Delta t} - M C_p T \Big _t$ |

$$\text{In} - \text{Out} = \text{Accumulation}$$

Thus  $\sum I - \sum O = \sum A.$

The heat balance equation thus becomes.

$$\rho \cdot V \cdot C_p \frac{dT}{dt'} = \rho F C_p \lambda (T_F - T) + V(-\Delta H) R_c - A A (T - T_c) \quad 1.5.8$$

$$\frac{dT}{dt'} = \left( \frac{F \lambda}{V} \right) (T_F - T) + \left( \frac{-\Delta H}{\rho C_p} \right) R_c - \frac{A A}{\rho V C_p} (T - T_c)$$

but  $\frac{dT}{dt'} = \frac{dy}{dt} \frac{dt}{dt'} \frac{dT}{dy}$  chain rule

$$= \left( \frac{dy}{dt} \right) \left( \frac{1}{T} \right) \left( \frac{T_F}{\gamma} \right)$$

$$\frac{dT}{dt'} = \frac{dy}{dt} \cdot \left( \frac{F \lambda T_F}{V \gamma} \right)$$

Hence from 1.5.8 it follows that

$$\frac{dy}{dt} = -\gamma + \left\{ \frac{(-\Delta H) C_F \gamma}{\rho C_p T_F} \right\} R \left\{ \frac{V}{\lambda F} \right\} \frac{C}{C_F} \quad 1.5.9$$

$$- \left\{ \frac{A \cdot A \cdot V}{\rho \cdot V \cdot C_p \cdot F \cdot \lambda} \right\} \gamma \cdot \left\{ \frac{T - T_c}{T_F} \right\}$$

$$\text{Let } \alpha = \left\{ \frac{(-\Delta H) C_F \delta}{\rho C_p T_F} \right\}$$

$$\text{and } \beta = \left\{ \frac{R \cdot A \tau}{\rho V C_p} \right\}$$

Therefore

$$\frac{dy}{dt} = -y + \alpha \cdot R \tau \left( \frac{C}{C_F} \right) - \beta (y - y_c)$$

Hence, the two dimensional system of ordinary non linear differential equations evolves as

$$\begin{aligned} \dot{y} &= -y + \alpha \delta (1-x) \exp\left(\frac{y}{1+y/\delta}\right) - \beta (y - y_c) \\ \dot{x} &= -x + \delta (1-x) \exp\left(\frac{y}{1+y/\delta}\right) \end{aligned} \quad 15.10$$

$\alpha, \beta, \delta, \delta, y_c$  constants

Note 1) The recycle rate  $(1-\lambda)$  influences the residence time  $\tau = (V/F \cdot \lambda)$  and only  $\alpha$  and  $\beta$  depend directly upon  $\tau$ .

2) This model is without feedback control which is extensively discussed in Appendix D.

## CHAPTER TWO

### 2 EXISTENCE, UNIQUENESS AND BOUNDEDNESS OF SOLUTIONS

2.1 This section gives, with proof, the domain within which the existence and uniqueness of solutions to the two dimensional system of ordinary differential equations below are assured.

$$\begin{aligned} \text{Given: } \dot{x} &= -x + \delta(1-x) \exp\left(\frac{y}{1+y/\delta}\right) \\ \dot{y} &= -y + \alpha \delta(1-x) \exp\left(\frac{y}{1+y/\delta}\right) - \beta(y-y_c) \end{aligned} \quad 2.1.1$$

$$\begin{aligned} \text{Recall: } x &= \left(\frac{C_F - C}{C_F}\right) \\ \text{and: } y &= \left(\frac{T - T_F}{T_F}\right) \delta \end{aligned} \quad 2.1.2$$

Intuitively, the physical domains of  $C$ ,  $T$ ,  $x$ , and  $y$  would be as follows.

|                        |
|------------------------|
| $0 < C \leq C_F$       |
| $0 < T < \infty$       |
| $0 \leq x < 1$         |
| $-\delta < y < \infty$ |

Table 2.1.1

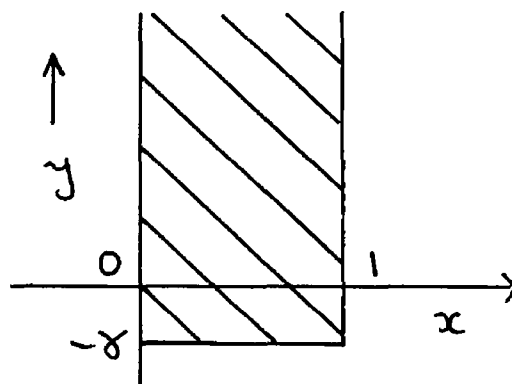


Fig. 2.1.1

This autonomous system may be abbreviated to

$$\dot{x} = f_1(x, y) \quad 2.1.3$$

$$\dot{y} = f_2(x, y) \quad 2.1.4$$

which may be represented in vector notation

$$\underline{\dot{X}} = \underline{F}(x, y) \quad 2.1.5$$

Lemma 2.1.1 For any  $\varepsilon > 0$  the function  $F(x, y)$  is continuously differentiable on the domain  $D_\varepsilon = [0, 1] \times [-\alpha + \varepsilon, \infty)$ . 2.1.6

Proof 2.1.1 The only potentially singular point is, if the denominator in the function  $\exp\left(\frac{y}{1+y/\alpha}\right)$  attains a zero value. This occurs only at  $y = -\alpha$  which is outside of  $D_\varepsilon$ . Hence  $F(x, y)$  is continuously differentiable on  $D_\varepsilon$  Q.E.D.

Theorem 2.1.2 For any initial condition  $(x(0), y(0))$  on  $D_\varepsilon$  the system  $\underline{x} = F(x, y)$  admits a unique local solution  $(x(t), y(t))$  for  $t$  in some time interval  $[0, \tau]$ .

Proof 2.1.2 Immediate; from lemma 2.1.1 and the classical existence and uniqueness theorem on O.D.E.'s as stated below and referenced from Chapter 6, section 1 of Sanchez.<sup>(2)</sup> Q.E.D.

Existence and Uniqueness Theorem.

Given the equation  $(*) \underline{x} = F(x, y)$  defined and continuous in the domain  $D_\varepsilon$  contained in  $\mathbb{R}^2$  and furthermore the partial derivatives  $\frac{\partial F}{\partial x}, \frac{\partial F}{\partial y}$ ,  $i=1, 2$  are defined and continuous on  $D_\varepsilon$ , then for every point  $(x(0), y(0))$  in  $D_\varepsilon$  there exists a unique solution  $(x(t), y(t))$  of  $(*)$  satisfying the initial condition  $\underline{x}(0) = (x(0), y(0))$  and defined in its neighbourhood.

The proof of local existence and uniqueness of solution is based on the method of successive approximations which formulates a converging sequence to the solution <sup>(2)</sup>

Uniqueness of solutions is of importance, if for instance, one wishes to approximate a solution numerically. If two solutions  $x = \phi(t)$  and  $x = \psi(t)$  of the equation  $\dot{x} = F(x, y)$  both satisfy  $\phi(t_0) = \psi(t_0) = x_0$ , the initial condition, then these solutions are identical in their common interval of definition  $D_\epsilon$ . The previous theorem gives sufficient conditions for the existence and uniqueness of solution of the first order equation.

**Lemma 2.1.3** The domain  $D_\epsilon$  is invariant under the evolution determined by the system 2.1.1 namely that for any initial condition  $(x(0), y(0))$  on  $D_\epsilon$  the corresponding local solution  $(x(t), y(t))$  remains in  $D_\epsilon$  for  $t < T$ .

**Proof 2.1.3** It suffices to check that the vector field  $F(x, y)$  points inwards on the boundary of the domain  $D_\epsilon = [0, 1] \times [-x + \epsilon, \infty)$ . 3)

Let us examine the behaviour of  $\dot{x}$  and  $y$  on the bounds of  $D_\epsilon$ .

$$\text{For } f_1(x, y) = -x + \delta(1-x) \exp\left(\frac{y}{1+y/\delta}\right) \quad 2.1.7$$

$$\text{Then } f_1(0, y) = \delta \left( \exp\left(\frac{y}{1+y/\delta}\right) \right) > 0 \quad 2.1.8$$

$$\text{And } f_1(1, y) = -1 < 0 \quad 2.1.9$$

Graphically this is represented overleaf in Fig. 2.1.2



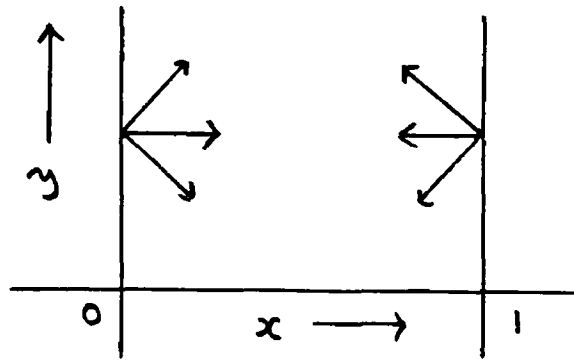


Fig. 2.1.2

Thus  $x(t) \in [0,1] \forall t \in [0,t_1)$

Continuity of  $f_1(x,y)$  implies that  $x(t)$  is bounded away from the boundary for  $t \in [0,T]$ .

A singularity of  $f_1$  and  $f_2$  occurs at  $y = -\alpha$ . One thus needs to examine  $\dot{y}(x,y)$  close to  $y = -\alpha$ .

Evaluate  $\dot{y}(x,y)$  for  $y$  in the neighbourhood of  $-\alpha$ .

$$\text{Let } y = -\alpha(1-\epsilon) \quad \text{where } \epsilon > 0, \quad \epsilon \text{ small.} \quad 2.1.10$$

$$\therefore \dot{y} = \alpha(1-\epsilon) + \alpha \delta(1-\alpha) \exp(-\alpha f(\epsilon)) + \beta \alpha(1-\epsilon) + \beta y_c$$

$$\text{Where } f(\epsilon) = \left( \frac{1-\epsilon}{\epsilon} \right) \quad 2.1.11$$

$$f(\epsilon) \xrightarrow{\epsilon \rightarrow 0} \infty$$

$$\text{And } \lim_{y \rightarrow -\alpha} \dot{y} = \alpha(1+\beta) + \beta y_c > 0 \quad 2.1.12$$

because  $\alpha, \beta, T_c$  and  $T_f$  are all positive.

Therefore,  $y$  is always bounded away from  $y = -\alpha$  which in itself is the only singularity point for this system on

$$D = [0,1] \times [-\alpha, \infty). \quad 2.1.13$$

An alternative approach to the invariance of the system of O.D.E.'s may be briefly summarized as follows: 11)

Rewriting the system in the following manner.

$$\frac{d}{dt}(e^t \cdot x) = e^t \cdot f(x, y) \quad 2.1.14$$

$$\frac{d}{dt}(e^{t(1+\beta)} \cdot y) = e^{t(1+\beta)} \cdot \alpha f(x, y) + e^{t(1+\beta)} \cdot \beta \cdot y_c \quad 2.1.15$$

$$\text{where } f(x, y) = \delta(1-x) \cdot \exp\left(\frac{y}{1+y/\delta}\right) \quad 2.1.16$$

Substitution and integration directly yield

$$\begin{aligned} y(t) - \alpha x(t) - \frac{\beta y_c}{1+\beta} &= \left( y(0) - \alpha x(0) - \frac{\beta y_c}{1+\beta} \right) \cdot e^{-t(1+\beta)} \\ &= -\alpha(1+\beta) \int_0^t e^{(1+\beta)(\tau-t)} \cdot x(\tau) d\tau \end{aligned} \quad 2.1.17$$

Since  $x(t) \in [0, 1]$  then the above equation implies that  $y(t)$  is also uniformly bounded.

Theorem 2.1.4  $\forall (x(0), y(0))$  in  $D_\varepsilon$ ,  $\exists M < \infty$  and  $L > -\delta$  such that the local solution  $(x(t), y(t))$ ,  $t < T$ , originating at  $(x(0), y(0))$  remains inside the compact set  $D_{L,M} = [0, 1] \times [L, M]$  for  $t < T$

$$\text{Moreover} \quad M = \max(y(0), y_u) \quad 2.1.18$$

$$\text{where} \quad y_u = \frac{\beta y_c + \alpha \delta e^\delta}{1 + \beta} \quad 2.1.19$$

$$\text{And} \quad L = \min(y(0), y_L) \quad 2.1.20$$

$$\text{where} \quad y_L = \frac{\beta y_c}{1 + \beta} \quad 2.1.21$$

Proof 2.1.4 Intuitively, one may examine the behaviour of  $y(x, y)$  as a function of  $x$  and  $y$  with the aid of Fig. 2.1.3 below

$$\dot{y} = -y(1 + \beta) + \beta y_c + \alpha \delta (1 - x) \exp\left(\frac{y}{1 + y/\delta}\right) \quad 2.1.22$$

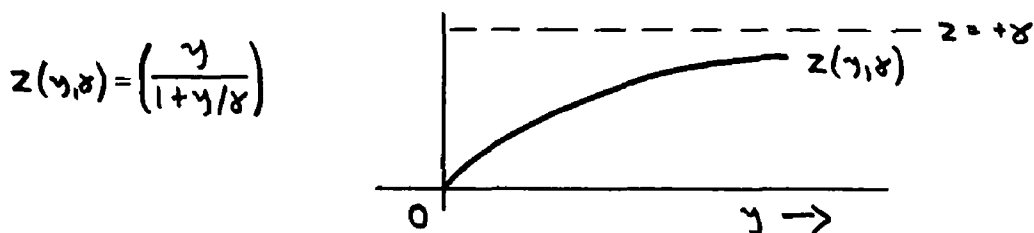


Fig. 2.1.3

Upper bound value  $y_u$

The max value of  $\alpha \delta (1 - x) \exp\left(\frac{y}{1 + y/\delta}\right)$

is  $\alpha \delta \exp \delta$

for  $y \geq y_u$  then  $\dot{y}(x, y) < 0$

Lower bound value  $y_L$

for  $y \leq y_L$  then  $\dot{y}(x, y) > 0$

Hence if the initial condition is outside these bounds then the local solution is driven towards this closed region and  $(x(t), y(t))$  will remain inside  $D_{L,M}$

Q.E.D

This conclusion may be represented graphically below:

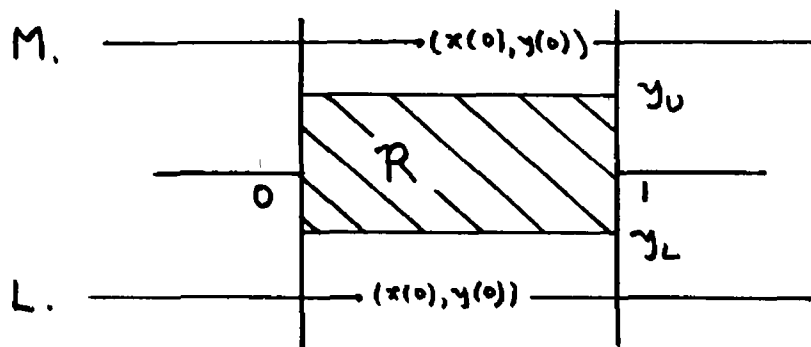


Fig 2.1.4

Trajectories  $(x(t), y(t))$  will tend towards the bounded region.

Steady state solutions can only exist within this region (R). Moreover, local solutions remain within the compact subset  $D_{L,M}$ .

It will be shown later in section 4.1 that all steady solutions including periodic solutions must lie within R and that this region could be further modified, if required.

**Theorem 2.1 5** For any initial condition  $(x(0), y(0))$  on  $D_{\mathcal{E}}$  the system  $\dot{X} = F(x, y)$  admits a unique global solution  $(x(t), y(t))$ ,  $t \geq 0$

**Proof 2.1.5** By Theorem 2.1.4, the local solution  $(x(t), y(t))$  is confined in the compact set  $D_{L,M} = [0, L] \times [L, M]$ .

where  $L = \min(y(0), y_L)$   
 and  $M = \max(y(0), y_u)$   
 and  $D_{L,M} \subset D_{\mathcal{E}}$ .

The proof of a unique global solution is given in "Differential Equations, Dynamical systems and linear Algebra" by Morris Hirsh/Stephen Small, Chapter 8, Section 5, p. 172. 3)

## CHAPTER THREE

### 3 LOCAL PROPERTIES

#### 3.1 EXISTENCE OF EQUILIBRIA.

Steady states, or critical points, exist when

$$x = y = 0 \quad 3.1.1$$

$$\text{This occurs when } x_s = \delta(1-x_s) \exp\left(\frac{y_s}{1+y_s/\delta}\right) \quad 3.1.2$$

$$\text{and } y_s = \alpha \delta(1-x_s) \exp\left(\frac{y_s}{1+y_s/\delta}\right) - \beta(y_s - y_c) \quad 3.1.3$$

Subscript "s" refers to steady state solutions.

Combining 3.1.2 and 3.1.3 yields the steady state system

$$\delta = g(x_s) \text{ with } g(x_s) = \left(\frac{x_s}{1-x_s}\right) \exp\left(\frac{-(\alpha x_s + \beta y_c)}{1+\beta + \frac{1}{\delta}(\alpha x_s + \beta y_c)}\right) \quad 3.1.4$$

$$\text{and } y_s = \frac{\alpha x_s + \beta y_c}{1+\beta} \quad 3.1.5$$

**Theorem 3.1.1** For  $\alpha, \delta$  and  $1+\beta, > 0$  there is at least one solution  $(x_s, y_s)$  to the steady state system.

**Proof 3.1.1** From the boundedness of the steady solutions

$$x_s \in [0, 1]$$

$$\text{and } y_s \in [L, M] \quad \text{See 2.1.4}$$

Hence  $\exp\left(\frac{-y_s}{1+y_s/\delta}\right)$  is finite.

For any  $\delta \in [0, \infty)$   $\exists x_s \in [0, 1]$  which satisfies the steady state equation below, as a result of the "intermediate value theorem"

$$x_s = \delta (1 - x_s) \exp\left(\frac{y_s}{1 + y_s/\delta}\right).$$

Recall that the boundedness of  $(x(t), y(t)) \in D_{L,M}$  where  $D_{L,M} = [0, 1] \times [M, N(y(0), y_L), \text{Max}(y(0), y_0)]$  was outlined in Theorem 2.1.5

For clarity, a pictorial representation of the steady state solution  $x_s$  set will be given.

Given 
$$g(x_s) = \left(\frac{x_s}{1 - x_s}\right) \exp\left(\frac{-y_s}{1 + y_s/\delta}\right)$$

for  $x_s \in [0, 1]$  and  $y_s = \frac{\alpha x_s + \beta y_c}{1 + \beta}$

Required to show that  $\exists x_s$  such that for a finite  $\delta_f$  that

$$\delta_f = g(x_s) \text{ has at least one solution.}$$

Note: 1)  $g(0) = 0$

2)  $g(1) = \infty$

and 3)  $g(x_s)$  is continuously differentiable at least once on the domain.

Intuitively, as is represented graphically below a horizontal line  $\delta = \delta_f$  will intersect the function at least once.

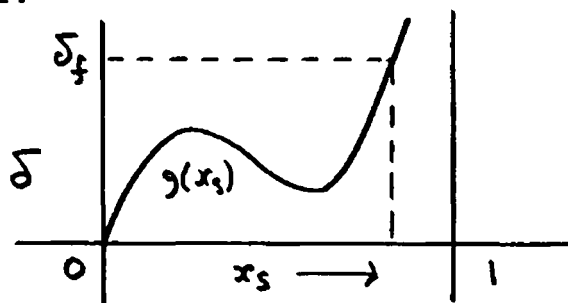


Fig. 3.1.1.

The question of multiplicity of steady states now naturally arises.

### 3.2

### MULTIPLICITY OF STEADY STATES.

For fixed values of  $\alpha, \beta, \gamma_c$ , the dependence of the steady state solution  $x_s$  on the Damkohler number,  $\delta$ , will have one of the few possible shapes shown below in Fig. 3.2.1

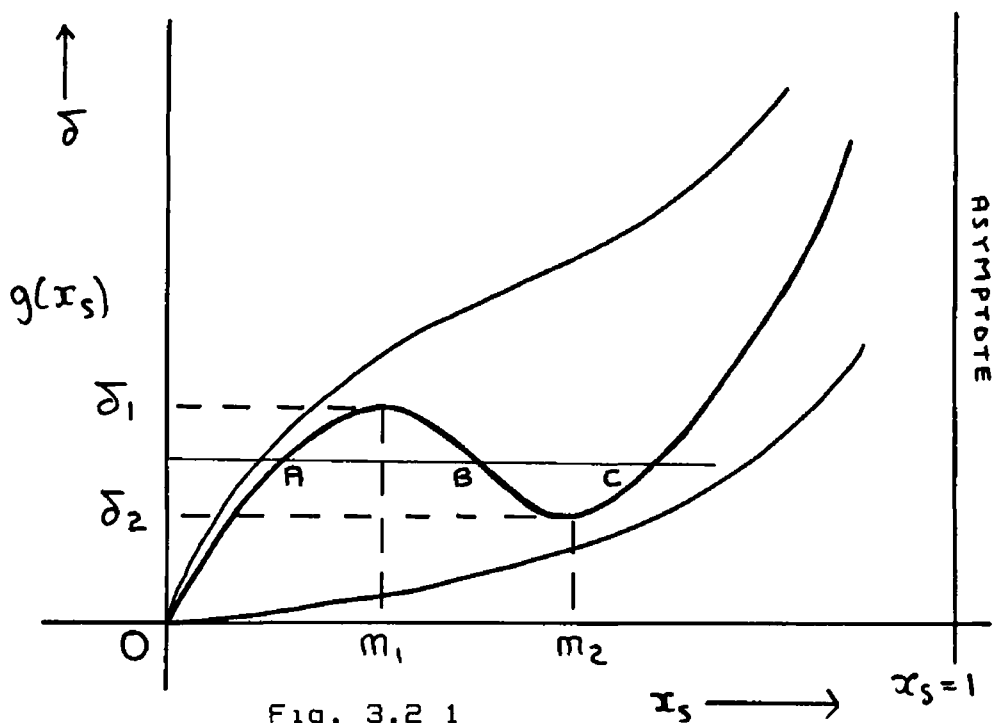


Fig. 3.2.1

If  $\delta_2 < \delta < \delta_1$  such that  $\frac{dg}{dx_s} < 0$  then three equilibria may occur as can be clearly seen e.g. points A, B, and C

Lemma <sup>13)</sup> 3.2.1 
$$\alpha \geq \left\{ \frac{4(1+\beta + \frac{\beta\gamma_c}{\delta})^2}{1+\beta - \frac{4}{\delta}(1+\beta + \frac{\beta\gamma_c}{\delta})} \right\} \quad 3.2.1$$

is a necessary condition for the existence of a multiplicity of steady states

Proof 3.2.1

$$\delta = g(x_s) = \frac{x_s}{1-x_s} \exp\left(\frac{-(\alpha x_s + \beta\gamma_c)}{1+\beta + \frac{1}{\delta}(\alpha x_s + \beta\gamma_c)}\right)$$

Evaluating  $\frac{dg}{dx_s} = 0$  gives two roots  $m_1, m_2$  which in order that they be real requires condition 3.2.1 above.

See Appendix [A] for more detailed calculations.

Given condition 3.2.1 and  $\sqrt{2} < \sqrt{\gamma} < \sqrt{1}$  , then  $\frac{dg}{dx_2} < 0$  when  $m_1 < x_2 < m_2$  . That is, three different equilibria theoretically may exist as steady state solution sets to a particular problem.

The nature of these equilibria however depends upon relationships between the parameters  $d, \beta, \gamma$ , AND  $y_c$  .



## 3.3

## STABILITY OF CRITICAL POINTS

The local stability character of the steady state solution can be determined by examining the sign of the real part of the eigenvalues of the Jacobian matrix <sup>1)</sup>

$$J = \begin{pmatrix} \frac{\partial f_1}{\partial x} & \frac{\partial f_1}{\partial y} \\ \frac{\partial f_2}{\partial x} & \frac{\partial f_2}{\partial y} \end{pmatrix}_{\substack{x=x_s \\ y=y_s}} \quad 3.3.1$$

$$J = \begin{pmatrix} \frac{-1}{1-x_s} & \frac{x_s}{(1+y_s/8)^2} \\ \frac{-dx_s}{1-x_s} & -(1+\beta) + \frac{dx_s}{(1+y_s/8)^2} \end{pmatrix} \quad 3.3.2$$

The eigenvalues  $\lambda_1, \lambda_2$  are given by the roots of the characteristic equation

$$\lambda^2 - (TR J)\lambda + (DET J) = 0 \quad 3.3.3$$

Mathematically it evolves that  $\frac{dy}{dx} < 0 \iff DET J < 0$

Hence the "slope" condition above defines steady states which are always unstable "SADDLE POINTS".

$$TR J = \left( \frac{-1}{1-x_s} \right) - (1+\beta) + \frac{dx_s}{(1+y_s/8)^2} \quad 3.3.4$$

$$\lambda_{1,2} = (TR J \pm \sqrt{\Delta}) / 2 \quad 3.3.5$$

$$\text{where } \Delta = (TR J)^2 - 4 DET J \quad 3.3.6$$

$DET J$  is quadratic in  $x_s$ , Roots at  $m_1, m_2$

$TR J$  is cubic in  $x_s$ .

The trace functions smallest root is negative, the other two roots are denoted by  $S_1, S_2$ .

See Appendix [B], for numerical evaluation of  $DET J$ , and  $TR J$  as functions of  $x_s$  at steady state.

The stability and nature of the critical points of the system are now summarised in the Table 3.3.1 overleaf.

| DET J     | $\Delta$     | Tr J          | NATURE OF CRITICAL PT | STABILITY |
|-----------|--------------|---------------|-----------------------|-----------|
| DET J < 0 |              |               | SADDLE                | UNSTABLE  |
| DET J > 0 | $\Delta < 0$ | Tr J $\neq 0$ | SPIRAL                | —         |
|           | $\Delta < 0$ | Tr J = 0      | CENTER                | STABLE    |
|           | $\Delta = 0$ |               | NODE                  | —         |
|           | $\Delta > 0$ |               | IMP NODE              | —         |
| DET J = 0 |              |               | DEGENERATE            | —         |

Table 3 3.1

Note: The spiral, proper and improper node, may be stable or unstable depending upon the sign of the trace of the Jacobian matrix

The second 'dynamic' stability condition is violated for those values of  $x_s$  at which  $\text{Tr J}$  takes on non negative values.

The points  $(s_1, s_2)$  where  $\text{Tr J} = 0$  defines the onset of instability

12)

Theorem 3.3.1 The critical points of the linear system may be classified as follows:

- 1) If  $\text{Det J} < 0$ , then the critical point is a saddle point. In the case of 3 critical points this condition may be strictly applied to the middle critical point.
- 2) If  $\text{Det J} > 0$ , the steady state is a spiral if  $\Delta < 0$  and  $\text{Tr J} \neq 0$ , a center if  $\Delta < 0$  and  $\text{Tr J} = 0$ , a proper node or an improper node if  $\Delta > 0$ .

The type of critical point for the non-linear problem is the same as that for the linear problem except in the case of a center which in the case of the non-linear problem it may be either a center or a spiral.

Recall that we proved in Theorem 2.1.4 that the trajectory is confined in a compact set: this in turn implies that if the system of O.D.E.'s exhibits a unique equilibrium then it is globally asymptotically stable.<sup>3)</sup> That is, for every initial condition  $x_0$  in  $\bar{D}_f$ , then

$$\lim_{t \rightarrow \infty} |x(t) - x_s| = 0 \quad 3.3.7$$

One may now characterise the stability and number of critical points for all parameters in this problem.

$$\text{Tr } J = \frac{-1}{1-x_s} - (1+\beta) + \frac{dx_s}{(1+y_s/\delta)^2} \quad 3.4.1$$

$$\text{DET } J = \frac{1+\beta}{1-x_s} - \left( \frac{dx_s}{(1+y_s/\delta)^2} \right) \quad 3.4.2$$

$$y_s = \frac{dx_s + \beta y_c}{1+\beta} \quad 3.4.3$$

$S_1, S_2$  are the middle and higher roots of  $\text{Tr } J = 0$ , the other root being always negative for this particular problem. See Appendix [C] for details.

$m_1, m_2$  are the roots of  $\text{DET } J = 0$

By comparing the relative values of the four roots  $m_1, m_2, S_1$  and  $S_2$  one may determine for any given  $x_s$  all permutations related to stability and multiplicity of solutions to this well posed problem.

Indeed this full classification is given overleaf in Table 3.4.1

| CLASS          | $m_1, m_2$                      | $s_1, s_2$                  | # OF CRITICAL POINTS                                             | RANGE OF ' $x_s$ '                               | NATURE OF CRITICAL POINT             |
|----------------|---------------------------------|-----------------------------|------------------------------------------------------------------|--------------------------------------------------|--------------------------------------|
| 1              | IMAGINARY                       | IMAGINARY OR $s_1, s_2 > 1$ | 1                                                                | $0 < x_s < 1$                                    | ASYMPTOTICALLY STABLE NODE OR SPIRAL |
| 2 <sub>a</sub> | $0 < m_1 < m_2 < 1$             | IMAGINARY                   | 1 if $\delta \in (0, \delta_2)$<br>if $\delta \in (\delta_1, 1)$ | $x_s < m_1 \cup x_s > m_2$                       | ASYMPTOTICALLY STABLE NODE OR SPIRAL |
| b              | $0 < m_1 < s_1 < s_2 < m_2 < 1$ |                             | 3 if $\delta_2 < \delta < \delta_1$                              | $m_1 < x_s < m_2$                                | SADDLE                               |
| 3              | $0 < m_1 < s_1 < m_2 < s_2 < 1$ |                             | 1                                                                | $x_s \in (0, m_1) \cup (s_1, 1)$                 | ASYMPTOTICALLY STABLE NODE OR SPIRAL |
|                |                                 |                             | OR                                                               | $x_s \in (m_1, m_2)$                             | SADDLE                               |
|                |                                 |                             | 3                                                                | $x_s \in (m_2, s_2)$                             | UNSTABLE SPIRAL OR NODE              |
| 4              | $0 < s_1 < m_1 < m_2 < s_2 < 1$ |                             | 1                                                                | $x_s \in (0, s_1) \cup (s_2, 1)$                 | ASYMPTOTICALLY STABLE NODE OR SPIRAL |
|                |                                 |                             | OR                                                               | $x_s \in (m_1, m_2)$                             | SADDLE                               |
|                |                                 |                             | 3                                                                | $x_s \in (s_1, m_1) \cup (m_2, s_2)$             | UNSTABLE SPIRAL OR NODE              |
| 5.             | IMAGINARY                       | $0 < s_1 < s_2 < 1$         | 1                                                                | $x_s \in (s_1, s_2)$                             | UNSTABLE SPIRAL OR NODE              |
|                |                                 |                             | 1                                                                | $x_s \in (0, s_1) \cup (s_2, 1)$                 | STABLE SPIRAL OR NODE                |
| 6              | $0 < m_1 < m_2 < s_1 < s_2 < 1$ |                             | 1                                                                | $x_s \in (0, m_1) \cup (m_2, s_1) \cup (s_2, 1)$ | STABLE SPIRAL OR NODE                |
|                |                                 |                             | OR                                                               | $x_s \in (s_1, s_2)$                             | UNSTABLE SPIRAL OR NODE              |
|                |                                 |                             | 3.                                                               | $x_s \in (m_1, m_2)$                             | SADDLE                               |

TABLE 341

## CHAPTER FOUR

### 4. BIFURCATION PHENOMENA

#### 4.1 PERIODIC BIFURCATION THEORY

Hopf Theorem for Vector Fields in  $\mathbb{R}^2$ .

THEOREM 2)

Consider the 2 - Dimensional differential system

$$\dot{\mathbf{z}} = \mathbf{F}_\delta(\mathbf{z}) \quad \text{where } (\mathbf{z}) = \begin{pmatrix} x \\ y \end{pmatrix} \quad 4.1.1$$

Let  $\bar{\mathbf{z}}_\delta$  be a  $\delta$  dependent equilibrium. Denote by  $A_\delta$  the Jacobian matrix of  $\mathbf{F}_\delta$  at  $\bar{\mathbf{z}}_\delta$  and by  $\rho(\delta) \pm i\omega(\delta)$  the eigenvalues of  $A_\delta$ . Suppose that for some value of  $\delta = \delta_c$  the following conditions hold.

$$\rho(\delta_c) = 0 \quad 4.1.2$$

$$\text{and } \frac{d}{d\delta} \rho(\delta_c) \neq 0 \quad \text{"STRICT CROSSING HYPOTHESIS". } 4.1.3$$

Then for every choice of a vector  $\mathbf{b}$  in  $\mathbb{R}^2$  there exists two differentiable functions

$$\Delta(-\epsilon, \epsilon) \rightarrow \mathbb{R} \quad \text{and} \quad \nabla(-\epsilon, \epsilon) \rightarrow \mathbb{R}$$

with  $\Delta(0) = 0$ ,  $\nabla(0) = 0$  such that for every  $s$  in  $(-\epsilon, \epsilon)$  the differential system  $\dot{\mathbf{z}} = \mathbf{F}_{\delta_c + s}(\mathbf{z})$  has a periodic solution of period  $\frac{2\pi}{\omega(\delta_c)} (1 + s \nabla(s))$  originating at  $\bar{\mathbf{z}}_{\delta_c} + s \mathbf{b}$

Moreover, the direction of bifurcation and the associated stability of the periodic solution can be explicitly determined from the sign of the two numbers  $\Delta'(0)$  and  $\frac{d}{d\delta} \rho(\delta_c)$ . A necessary condition for bifurcating orbits to be stable, is that these numbers have the same sign.

8)

A NOTE ON HOPF BIFURCATION.

HOPF BIFURCATION refers to the evolution of stable periodic orbits from a stable fixed point, as a parameter  $\delta$  crosses a critical value. The appearance of closed orbits is interpreted as a "shift of stability" from the original stationary solution. An initial condition near the original fixed point is attracted to and becomes indistinguishable from the closed orbit. See Fig. 4.1.1 below.

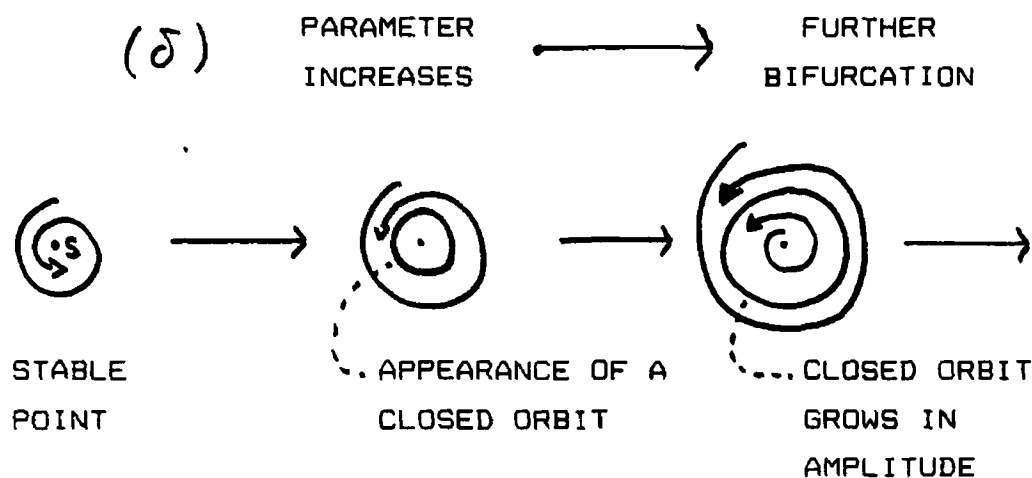


Figure 4.1.1  
The Hopf Bifurcation.

# APPLICATION OF THE HOPF THEOREM TO THE C.S.T.R.

Comment:-

$$\begin{aligned} \text{Given system 1, } \dot{x} &= -x + \delta(1-x) \exp\left(\frac{\gamma}{1+\gamma/\delta}\right), \\ \dot{\gamma} &= -\gamma + \alpha \delta(1-x) \exp\left(\frac{\gamma}{1+\gamma/\delta}\right) - \beta(\gamma - \gamma_c). \end{aligned} \quad 4.1.4$$

let the bifurcation parameter be  $\mu$ ;

$$\text{where } \mu = \delta - \delta_s \quad 4.1.5$$

$$\delta_s = \text{Damkohler constant at steady state.}$$

For  $X_\mu(0) = 0$  one must linearize system 1 around a steady state, i.e. let  $\hat{x} = x - x_s$ . However, this is equivalent to examining the Jacobian Matrix at  $\hat{x} = 0$ . 5)

i.e.  $dX_\mu(0,0)$  is equivalent to

$$J = \begin{pmatrix} \frac{-1}{1-x_s} & \frac{x_s}{(1+\gamma_s/\delta)^2} \\ \frac{-\alpha x_s}{1-x_s} & -(1+\beta) + \frac{\alpha x_s}{(1+\gamma_s/\delta)^2} \end{pmatrix} \quad 4.1.6$$

$$\text{where } \lambda_{1,2} = \text{Tr } J \pm \sqrt{(\text{Tr } J)^2 - 4 \text{Det } J}. \quad 4.1.7$$

For, complex eigenvalues this requires that

$$\text{Tr } J = 0 \quad 4.1.8$$

$$\text{and } \text{Det } J > 0 \quad 4.1.9$$

$$\text{where } \text{Tr } J = \left( \left( \frac{-1}{1-x_s} \right) - (1+\beta) + \frac{\alpha x_s}{(1+\gamma_s/\delta)^2} \right) \quad 4.1.10$$

$$\text{Det } J = \left( \frac{1+\beta}{1-x_s} - \frac{\alpha x_s}{(1+\gamma_s/\delta)^2} \right). \quad 4.1.11$$

$$\gamma_s = \left( \frac{\alpha x_s + \beta \gamma_c}{1+\beta} \right). \quad 4.1.12$$

$\text{Tr } J$  may be written as a "cubic" in  $x_s$ .

$\text{Det } J$  may be written as a "quadratic" in  $x_s$ .



## NO HOPF BIFURCATION WITHOUT COOLING

$\beta$  is a measure of the heat transfer coefficient between reactor and coolant whose normalised dimensionless temperature is  $y_c$ .

$\beta = 0$  corresponds to an adiabatic reactor; no cooling.

**Theorem 4.1.2** In system 1, there can be no periodic orbits when  $\beta = 0$ .

**Proof** 4.1.2 Given  $\dot{x} = -x + f(x, y)$  4.1.13

$$y = -y + d f(x, y) \quad 4.1.14$$

$$\text{where } f(x, y) = \delta \cdot (1-x) \exp(1+y/\delta). \quad 4.1.15$$

Combining equations 4.1.13 and 4.1.14 yields

$$d \cdot x - \dot{y} = -(d x - y). \quad 4.1.16$$

Let  $W(x, y) = d x - y. \quad 4.1.17$

Therefore  $\dot{W}(x, y) = -W(x, y). \quad 4.1.18$

Solution  $W = w_0 \cdot e^{-t} \quad 4.1.19$

but if  $x$  and  $y$  are periodic, with the same period, then  $W$  will be periodic. This is not true from eqt. 4.1.19, and hence no periodic solutions can exist without cooling.  
Q.E.D.

The only possible exception to " $W(x, y)$  not being periodic" is if  $w_0 = 0, \forall t$ .

and hence  $d x(t) = y(t) \quad \forall (x, y) \in D_\epsilon = [0, 1] \times [-\delta + \epsilon, \infty).$

Graphically this is represented thus by the line  $L: dx = y$ , as shown in Fig. 4.1.2

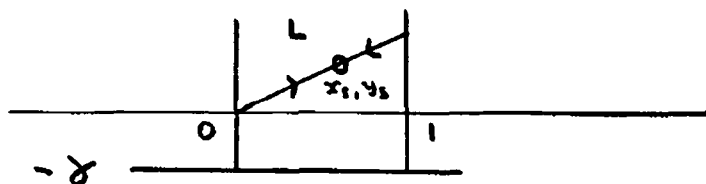


Fig. 4.1.2

However, a line cannot carry a periodic solution as this violates the theorem of the existence of a unique solution (2.1.2)

Thus  $W_0 = 0$  is also not a solution. Q.E.D.

Note: An alternative approach is to investigate the eigenvalues of the Jacobian Matrix  $J$ , which must be purely imaginary. For this to occur requires:  $\text{Tr } J = 0$  and  $\text{Det } J > 0$

However, for  $\beta = 0$ , setting  $\text{Tr } J = 0$  it follows that  $\text{Det } J = -1$ , and hence Hopf bifurcation will not be possible; Details are given below.

$$J_s = \begin{pmatrix} \frac{-1}{1-x_s} & \frac{x_s}{(1+y_s/\delta)^2} \\ \frac{-d x_s}{1-x_s} & -(1+\beta) + \frac{d x_s}{(1+y_s/\delta)^2} \end{pmatrix}$$

Let

$$\left. \begin{aligned} \phi &= \frac{-1}{1-x_s} \\ \beta &= 0 \\ w &= \frac{x_s}{(1+y_s/\delta)^2} \end{aligned} \right\} \text{for ease of calculation}$$

Thus

$$J_s = \begin{pmatrix} \phi & w \\ d(\phi+1) & -1+d w \end{pmatrix}$$

$$\text{Tr } J_s = \phi + d w - 1 = 0 \quad \text{as required}$$

Hence

$$\text{Det } J_s = -\phi - d w = -1.$$

$$\lambda^2 - (\text{Tr } J_s)\lambda + \text{Det } J_s = 0$$

$$\Rightarrow \lambda^2 - 1 = 0 \quad \text{hence} \quad \lambda_s = \pm 1, \text{ only.}$$

When  $\beta = 0$ , the roots of the characteristic equation are real and they can never be purely imaginary. Therefore, the formulation of periodic orbits due to HOPF BIFURCATION cannot occur.

Q.E.D.

# REGIONS WHERE PERIODIC SOLUTIONS CANNOT OCCUR

Theorem 4.1.3 Whenever  $(x(t), y(t))$  is a periodic orbit  
 then  $\frac{\beta y_c}{1+\beta} \leq y(t) \leq \frac{\alpha \delta \exp(\delta) + \beta y_c}{1+\beta}$

Proof 4.1.3 From system 1,

$$\begin{aligned} \dot{y} &= -y + \alpha \delta (1-x) \exp\left(\frac{y}{1+y/\delta}\right) - \beta(y - y_c) \\ &= -y(1+\beta) + \beta y_c + \alpha \delta (1-x) \exp\left(\frac{y}{1+y/\delta}\right) \end{aligned}$$

A) When  $y_c = \frac{\beta y_c}{1+\beta} = y_L$   
 then  $\dot{y} = \alpha \delta (1-x) \exp\left(\frac{y}{1+y/\delta}\right) \geq 0 \quad \forall x \in [0,1]$   
 for  $y < y_L$  then  $\dot{y} > 0$

B) When  $y_u = \frac{\alpha \delta \exp(\delta) + \beta y_c}{1+\beta} = y_u$   
 then  $\dot{y} = \alpha \delta (1-x) \exp\left(\frac{y}{1+y/\delta}\right) - \exp(\delta) < 0 \quad \forall x \in [0,1]$   
 for  $y > y_u$  then  $\dot{y} < 0$

These upper and lower bounds may be represented graphically as shown below in Fig. 4.1.3

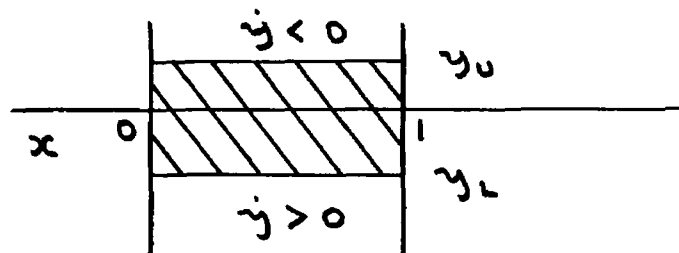


Fig. 4.1.3

No periodic solutions are possible outside of the shaded area. It should be noted however, that  $y_u$  and  $y_L$  may be refined further. Q.E.D.

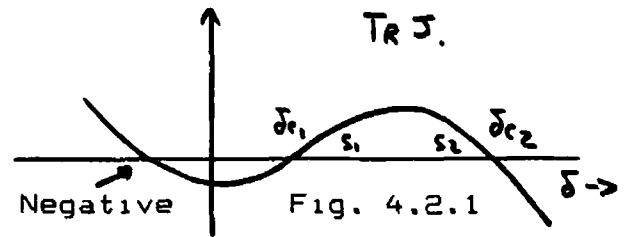
The significance of these upper and lower bounds will be clearly seen in the phase portrait solutions numerically evaluated by a NAG computer programme, which are documented in Chapter 5.

## A "Sample" Explanation on Stability.

The characteristic equation of a 2 - Dimensional Jacobian Matrix is

$$\lambda^2 - (\text{Tr } J)\lambda + \text{Det } J = 0. \quad 4.2.1$$

A typical plot of the Trace function is shown for the C.S.T.R. model. in Fig. 4.2.1



Note:  $\frac{\text{Tr } J_s}{2} = f(\delta_s) = 0$   
at  $\delta_s = \delta_{ci}, i = 1, 2.$

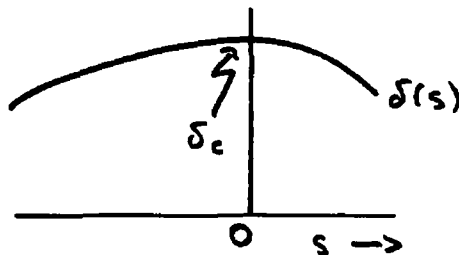
A detailed phase plot may be obtained close to where the Trace of the Jacobian vanishes by reparameterizing  $\delta_s$  in the neighbourhood of  $\delta_c$  as follows

$$\delta(s) = \delta_c + s \cdot \Delta(s).$$

Then, linearizing about  $s = 0$ , yields from TAYLORS THEORY

$$\delta_s - \delta_c \simeq s^2 \Delta'(0) + o(s^2) \text{ as } s \rightarrow 0$$

For  $\Delta'(0) < 0$  a typical plot of the above expression would be as follows in Fig. 4.2.2



$$\Delta'(0) < 0 \Rightarrow \delta_s < \delta_c.$$

Fig. 4.2.2

Hence periodic solutions to this differential system in the neighbourhood of  $\delta_c$  would be possible only for  $\delta_s < \delta_c$  as is shown diagrammatically overleaf in Fig. 4.2.3.

In this example, if

$$\Delta'(0) < 0$$

$$\Rightarrow \delta(s) < \delta_c$$

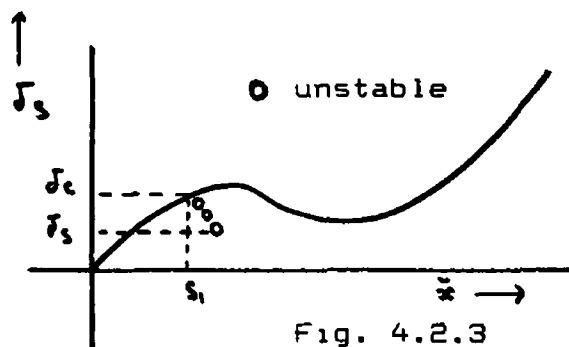


Fig. 4.2.3

However, bifurcation is normally described as being "to the left" <sup>13)</sup> by reference to the conventional bifurcation diagram where the bifurcation parameter  $\delta$  is the first variable. See Fig. 4.2.4 below. In any event the periodic orbits will necessarily be unstable.

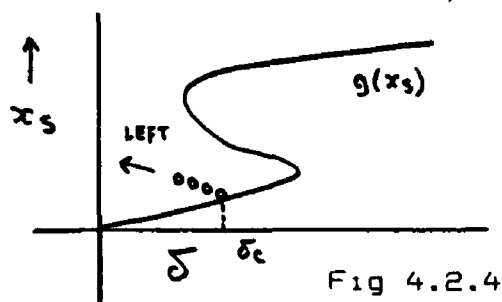


Fig 4.2.4

The last condition of the theorem shows that there is a direct link between the direction of bifurcation and the stability of the bifurcating orbit

A phase diagram for  $(x(t), y(t))$ , when  $\delta_s$  is 'close to'  $\delta_c$ , about a critical point  $(s)$  would be as follows in Fig. 4.2.5.

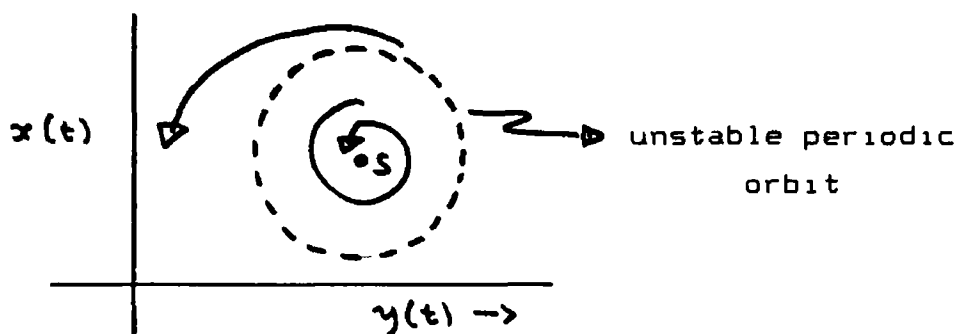


Fig. 4.2.5

This example of an unstable closed orbit is also referred to as "SUBCRITICAL BIFURCATION". <sup>8)</sup>

Development of a stable closed orbit, known as SUPERCRITICAL BIFURCATION is shown below in Fig. 4.2.6. This evolution of periodic solutions is strictly Hopf Bifurcation.

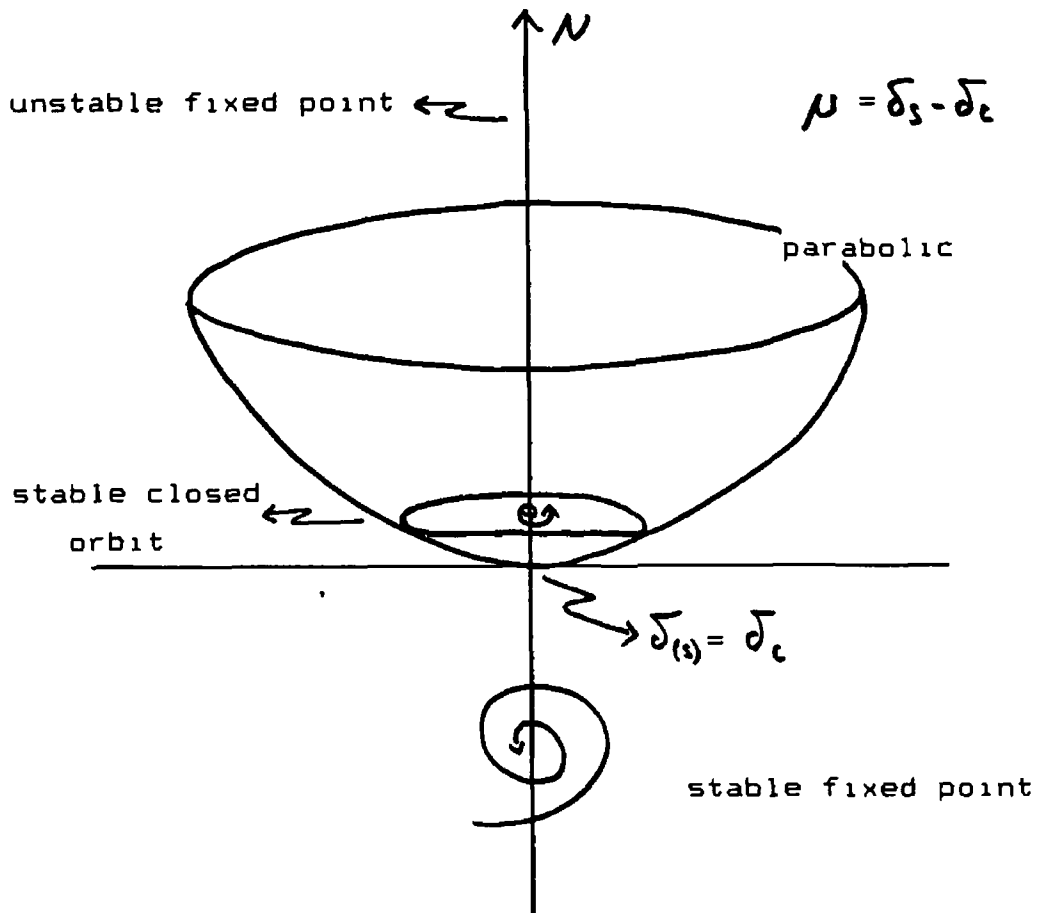


Fig. 4.2.6

For  $\mu$  in the neighbourhood of  $\mathcal{E}$ , the radius of the closed orbit is proportional to  $\sqrt{\mu}$ .

$\mu$  is a perturbation parameter.

Bifurcation occurs at  $\mu = 0$

A pictorial summary of the nature of bifurcating orbits and their relationship to the salient parameters is now given overleaf in Table 4.2.1.

A)  $\Delta'(0) > 0$

|                    |                                                                                                          |                                                                                                                                               |
|--------------------|----------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------|
| $f'(\delta_c) > 0$ | $\delta < \delta_c$<br> | $\delta > \delta_c$<br> $\begin{matrix} * \\ S \end{matrix}$ |
| $f'(\delta_c) < 0$ | $\delta < \delta_c$<br> | $\delta > \delta_c$<br> $\begin{matrix} * \\ U \end{matrix}$ |

B)  $\Delta'(0) < 0$

|                    |                                                                                                                                                 |                                                                                                            |
|--------------------|-------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------|
| $f'(\delta_c) > 0$ | $\delta < \delta_c$<br> $\begin{matrix} * \\ U \end{matrix}$   | $\delta > \delta_c$<br>   |
| $f'(\delta_c) < 0$ | $\delta < \delta_c$<br> $\begin{matrix} * \\ S \end{matrix}$ | $\delta > \delta_c$<br> |

Table 4.2.1

As can be seen for four out of the eight cases no bifurcation to periodic orbits occurs.

Of the remaining four examples, two critical points are surrounded by stable orbits the other two are surrounded by unstable orbits

Intuitively, the following condition is necessary for stability of bifurcating periodic orbits - i.e.  
SUPERCRITICAL BIFURCATION.

$\Delta'(0)$  AND  $\frac{d}{d\delta} f(\delta_c)$  MUST HAVE THE SAME SIGN  
SEE  FOR STABILITY CONDITION

## 4.3

## DEVELOPMENT OF HOPFS BIFURCATION THEORY

For the 2 dimensional autonomous system it is desirable to write it in the following form

$$\frac{dW}{d\tau} = A^0 W + S G(W, S) \quad 4.3.1$$

where  $S$  is a small parameter  
and where  $A^0$  has purely imaginary eigenvalues.

Given  $S$  as the bifurcation parameter; then to achieve the necessary formulation above, one reparameterizes the original differential system

$$\dot{\bar{z}} = F_{\delta}(\bar{z}) \quad \text{as follows}$$

$$\text{let } \bar{z}_{\delta_s} = \bar{z}_{\delta_c} + s \Delta(s) \quad \begin{array}{l} \text{Equilibrium solutions} \\ \text{close to criticality, } C. \end{array}$$

$$\tau = \frac{T}{T_s} \cdot t. \quad \text{Magnified time function.}$$

$$T_s = T (1 + \tau(s) S)$$

$$W(\tau) = \left( \frac{z(\tau) - \bar{z}_{\delta_s}}{S} \right) \quad \begin{array}{l} \text{Magnified view of a} \\ \text{solution in the} \\ \text{neighbourhood of a} \\ \text{bifurcation point.} \end{array}$$

$$A_{\delta_c} = J(F_{\delta}, \bar{X}_{\delta}) \quad \begin{array}{l} \text{Jacobian function when} \\ \delta = \delta_c \text{ the trace vanishes.} \end{array}$$

$$C_{\delta} = \frac{A_{\delta} - A_{\delta_c}}{\delta - \delta_c}$$

$$C_0 = \left. \frac{d}{d\delta} A_{\delta} \right|_{\delta = \delta_c}$$

$$\text{and } Q^S(W) = \frac{F^S(\bar{z} + sW) - S \cdot A_{\delta_s} \cdot W}{s^2} \quad 4.3.2$$



Introducing the new variables, the original differential system may be reformulated as follows

$$\begin{aligned}
 \frac{d}{d\tau} W(\tau) &= \frac{1}{S} \frac{d}{d\tau} Z(\tau) = \frac{T_S}{T} \cdot \dot{Z} \\
 &= \left( \frac{1 + S \nabla(s)}{S} \right) F^S(Z). \\
 &= \left( \frac{1 + S \cdot \nabla(s)}{S} \right) \cdot \left( S A_\delta W + S^2 Q_{\delta_S} W \right). \\
 &= A^S W + S \left( \nabla(s) A^S W + (1 + \nabla(s)) Q_S W \right). \\
 \therefore W(\tau) &= A^0 W + S \left( \Delta(s) \dot{C} W + \nabla(s) A^S W + (1 + \nabla(s)) \dot{Q} W \right) \quad 4.3.3
 \end{aligned}$$

This differential system is now in the desired format, and the solution by the method of variation of parameters is

$$W(\tau, s) = e^{\tau A^0} b + s e^{\tau A^0} \int_0^\tau e^{-\tau A^0} \left[ \Delta(s) \dot{C} W + \nabla(s) A^S W + (1 + \nabla(s)) \dot{Q} W \right] d\tau.$$

This solution is  $T$  periodic, and

$$\Delta(s), \nabla(s) \in C'(-\varepsilon, \varepsilon), \quad \Delta(0) = 0 = \nabla(0).$$

Thus the original system

$$\dot{Z}(t) = F^S(Z_t) \quad \text{has a } T_S \text{ periodic solution}$$

$$Z(t) = \bar{Z}^{(s)} + S W\left(\frac{T}{T_S} t, s\right) \quad 4.3.4$$

which is stable, iff  $\Delta'(0) > 0$  at  $\delta_{c_1}$   
iff  $\Delta'(0) < 0$  at  $\delta_{c_2}$

Continuity properties of  $W(\tau, s)$  now directly lead to the following proposition.

PROPOSITION 4.3.1

ii)

The solution  $W(\tau, s)$  can be expanded in  $S$  as

$$W(\tau, s) = W(\tau, 0) + s W_1(\tau) + s^2 W_2(\tau, s) \quad 4.3.5$$

where  $W(\tau, 0) = e^{\tau A} b$ .

$$W_1(\tau) = e^{\tau A} \int_0^\tau e^{-\tau A} Q^0(W(\tau, 0)) d\tau$$

$$W_2(\tau, s) \xrightarrow{s \rightarrow 0} 0$$

Thus, it is possible to evaluate  $W(\tau, s)$  in the neighbourhood of  $S = 0$ .

Since  $W(\tau, s)$  and  $e^{\tau A^0}$  are both  $T$  periodic, then expression 4.3.3 yields

$$\Delta(s) \int_0^T e^{-\tau A^0 s} W(\tau, s) d\tau + \Gamma(s) \int_0^T e^{-\tau A^0 s} A W(\tau, s) d\tau + (1 + s\Gamma(s)) \int_0^T e^{-\tau A^0 s} Q(W(\tau, s)) d\tau = 0 \quad 4.3.6$$

Equating terms of first order in  $S$ , gives

$$\Delta'(0) \int_0^T e^{-\tau A^0} e^{\tau A^0} b d\tau + \Gamma'(0) \int_0^T e^{-\tau A^0} A e^{\tau A^0} b d\tau + \int_0^T e^{-\tau A^0} \left( \frac{d}{ds} Q(W(\tau, s)) \right) \Big|_{s=0} d\tau = 0 \quad 4.3.7$$

From the above equation it will be possible to determine explicitly the  $\Delta'(0)$  function, including its sign. Thus the stability of periodic orbits in the neighbourhood of  $\delta c_i$ ,  $i = 1, 2$  may be evaluated.

However, the first two integral expressions in equation 4.3.7 may be simplified further.

$$a) \quad I_1 = \int_0^T e^{-\tau A^0} A^0 e^{\tau A^0} b \, d\tau = T A^0 b. \quad 4.3.8$$

$$b) \quad I_2 = \int_0^T e^{-\tau A^0} c^0 e^{\tau A^0} b \, d\tau = \frac{T}{2} \left( c^0 - \frac{1}{2\omega_0} A^0 c^0 A^0 \right) b. \quad 4.3.9$$

Simplification in case b is obtained as follows.

Since the eigenvalues of  $A^0$  are  $\pm i\omega_0$ , then

$$A^0 = R \cdot D \cdot R^{-1}$$

$$\text{with } D = \begin{pmatrix} i\omega_0 & 0 \\ 0 & -i\omega_0 \end{pmatrix}$$

and  $R$  = Some invertible matrix.

$$\begin{aligned} \text{Hence } e^{\tau D} &= \begin{pmatrix} e^{i\tau\omega_0} & 0 \\ 0 & e^{-i\tau\omega_0} \end{pmatrix} \\ &= \cos \tau\omega_0 \cdot I + \frac{\sin \tau\omega_0}{\omega_0} \cdot D \end{aligned} \quad 4.3.10$$

$$\text{Thus } I_2 = \int_0^T \left( \cos \tau\omega_0 \cdot I - \frac{\sin \tau\omega_0}{\omega_0} A^0 \right) c^0 \left( \cos \tau\omega_0 \cdot I + \frac{\sin \tau\omega_0}{\omega_0} A^0 \right) b \, d\tau$$

which yields the result outlined in (b) above.

Simplification of these 2 integrals yields the following general expression

$$\Delta'(0) \frac{T}{2} \left( c^0 - \frac{1}{2\omega_0} A^0 c^0 A^0 \right) b + \nabla'(0) T A^0 b + \int_0^T e^{-\tau A^0} \frac{d}{ds} \left( Q^s(w(\tau, v)) \right) \Big|_{s=0} d\tau = 0 \quad 4.3.11$$

As 'b' is a vector it may be suitably chosen for ease of calculation, as will be shown, such that  $\Delta'(0)$  may be readily evaluated.

#### 4.4 DIRECTION OF BIFURCATION

4.4.1 The previous section outlined the derivation from general theory of a specific analytical expression, the sign of which ascertains the direction of bifurcation and the associated stability of the periodic orbits of a 2 dimensional differential system.

In the case of this continuous stirred tank reactor model, inputting numerical data for the constants  $\alpha, \beta, \gamma, \delta$  and  $\gamma_c$  still results in a very detailed calculation in order to evaluate the sign of  $\Delta'(0)$ ; the desired result.

The ensuing derivations are pioneered by the author for the more complex case of  $\gamma$  finite.

Again, the object of this analysis is to evaluate the sign of  $\Delta'(0)$  from the following expression.

$$\Delta'(0) \frac{T}{2} (c^0 - \frac{1}{w_0^2} A^0 c^0 A^0) b + \overline{V}(0) T A^0 b + \int_0^T e^{-\tau A^0} \frac{d}{ds} (Q^3(w(\tau, s))) \Big|_{s=0} d\tau = 0 \quad 4.4.1$$

Indeed, the second term involving  $\overline{V}(0)$  will be eliminated from the calculations as it will be shown later that this is possible by a suitable choice of the vector b.

The calculations are consequently divided now into two parts;

$$\text{Evaluating a) } \frac{T}{2} (c^0 - \frac{1}{w_0^2} A^0 c^0 A^0) \quad 4.4.2$$

$$\text{b) } \int_0^T e^{-\tau A^0} \frac{d}{ds} (Q^3(w(\tau, s))) \Big|_{s=0} d\tau \quad 4.4.3$$

4.4.2 To evaluate  $\frac{T}{2} \left( c^0 - \frac{1}{\gamma_0} A^0 c^0 A^0 \right)$  for  $\delta$  finite.

The vector field is represented by the expression,

$$F_{\delta}(\bar{z}) = \begin{pmatrix} -x + \delta(1-x) e^{\frac{\delta y}{\delta+y}} \\ \beta y_c - (1+\beta)y + \delta(1-x) e^{\frac{\delta y}{\delta+y}} \end{pmatrix} \quad 4.4.4$$

A stationary point  $\bar{z} = \begin{pmatrix} \bar{x} \\ \bar{y} \end{pmatrix}$  is evaluated from,

$$\bar{y} = \frac{\delta \bar{x} + \beta y_c}{1+\beta}$$

$$\text{where } g(\bar{x}) = \left( \frac{x}{1-x} \right) e^{\frac{-\delta(\delta x + \beta y_c)}{\delta x + \beta y_c + (1+\beta)\delta}}$$

The Jacobian  $J_{\delta}(\bar{z})$  at equilibrium may be calculated to give,

$$J_{\delta}(\bar{z}) = \begin{pmatrix} \frac{-1}{1-x} & \left( \frac{\delta}{\delta+y} \right)^2 x \\ \frac{-\delta x}{1-x} & -(1+\beta) + \delta \left( \frac{\delta}{\delta+y} \right)^2 x \end{pmatrix}_{\substack{x=\bar{x} \\ y=\bar{y}}}$$

However the critical value of the Damkohler constant  $\delta_c$  is when the Trace of the Jacobian vanishes;

$$\text{Hence } J(\bar{z}_c) = A^0 = \begin{pmatrix} \frac{-1}{1-x} & \frac{1}{2}(1+\beta + \frac{1}{1-x}) \\ \frac{-\delta x}{1-x} & \frac{1}{1-x} \end{pmatrix}_{x=\bar{x}_c} \quad 4.4.5$$

The matrix  $c^0$  is defined as

$$\begin{aligned} c^0 &= \frac{d}{d\delta} \left( J(\bar{z}) \right)_{\delta=\delta_c} \\ &= \left( \frac{d}{d\bar{x}} J(\bar{z}) \frac{d\bar{x}}{d\delta} \right)_{\delta=\delta_c} + \left( \frac{d}{d\bar{y}} J(\bar{z}) \frac{d\bar{y}}{d\delta} \right)_{\delta=\delta_c} \\ &= \left( \frac{dJ}{d\bar{x}} + \frac{d}{\beta+1} \frac{dJ}{d\bar{y}} \right)_{\delta=\delta_c} \cdot \frac{1}{g'(\bar{x}_c)} \end{aligned} \quad 4.4.6$$

Straightforward differentiation yields

$$C^0 = \left( \begin{array}{cc} \frac{1}{(1-x)^2} & \frac{x^2}{(x+y)} - \frac{2dx^2x}{(1+\beta)(x+y)^3} \\ \frac{-d}{(1-x)^2} & \frac{dx^2}{(x+y)} - \frac{2d^2x^2x}{(1+\beta)(x+y)^3} \end{array} \right) \cdot \frac{1}{g'(x)} \Bigg|_{\substack{x=\bar{x}_c \\ y=\bar{y}_c}}$$

$$\text{where } g'(\bar{x}_c) = \left( \frac{1}{(1-x)^2} - \frac{d(1+\beta)x^2x}{(1-x)(dx+\beta y_c) + (1+\beta)x^2} \right) \frac{\bar{y}_c(1-x)}{x} \Bigg|_{x=\bar{x}_c}$$

$$= \frac{\bar{y}_c \text{DET } A^0}{(1+\beta) \cdot \bar{x}_c}$$

$$= \frac{\bar{y}_c w_0^2}{(1+\beta) \bar{x}_c}$$

4.4.7

Simplifying the notation :  
as follows;

$$\bar{x}_c = a$$

$$\text{Let } \frac{1}{1-\bar{x}_c} = b.$$

$$\frac{1}{\bar{x}+\bar{y}_c} = d$$

$$A = \begin{pmatrix} -b & \frac{b+1+\beta}{d} \\ -d & a b \end{pmatrix}$$

$$C = \begin{pmatrix} -b^2 & \bar{x}^2 d^2 - \frac{2d\bar{x}^2 a d^3}{1+\beta} \\ -d b^2 & d\bar{x}^2 d^2 - \frac{2d^2 \bar{x}^2 a d^3}{1+\beta} \end{pmatrix} \cdot \left( \frac{(1+\beta) a}{\bar{y}_c w^2} \right)$$

Clearly

$$A^0 \begin{pmatrix} 1 \\ 0 \end{pmatrix} = -b \begin{pmatrix} 1 \\ d a \end{pmatrix}$$

and a suitable choice of  $b = \begin{pmatrix} -da \\ 1 \end{pmatrix}$  will eliminate the  $\nabla^1(0) T A^0 b$  term from the general expression 3.2

Further calculations give

$$\frac{1}{2} \left( C^0 - \frac{1}{w_0} A^0 C^0 A^0 \right) \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{-ab(1+\beta)}{2\bar{y}_c w_0^3} \begin{pmatrix} 1 \\ d \end{pmatrix} + \frac{ab(1+\beta)}{2\bar{y}_c w_0^4} \left( -b^2 + d\bar{x}^2 a d^2 - \frac{2d\bar{x}^2 a d^3}{1+\beta} \right) \begin{pmatrix} \beta+1 \\ d \end{pmatrix} \quad 4.4.8$$

Using the relationship :

$$\begin{aligned} 1) b+1+\beta &= 2\gamma^2 a d^2 \\ 2) b((1+\beta)a-1) &= w^2 \end{aligned} \quad 4.4.9$$

and evaluating the scalar product of this vector with  $\begin{pmatrix} -da \\ 1 \end{pmatrix}$  gives, upon simplification;

$$\frac{1}{2} \left( \left( c^0 - \frac{1}{w_0^2} A^0 c^0 A^0 \right) \begin{pmatrix} 1 \\ 0 \end{pmatrix} \right) \cdot \begin{pmatrix} -da \\ 1 \end{pmatrix} = \frac{-da}{2} \text{Tr } c^0 \quad 4.4.10$$

This result is exactly equivalent to the infinite  $\delta$  case. <sup>11)</sup>

4.4.3 To evaluate  $\int_0^T e^{-\tau A^0} \frac{d}{ds} (Q^s(w(\tau, s))) \Big|_{s=0} d\tau$

where  $Q^s(w) = \frac{F_\delta(\bar{z} + h) - A(\bar{z})}{s^2} h$

and  $h = s \cdot w(\tau, s)$

$$\underline{w(\tau, s) = \begin{pmatrix} u(\tau, s) \\ v(\tau, s) \end{pmatrix} = \begin{pmatrix} u(\tau) \\ v(\tau) \end{pmatrix} + s \begin{pmatrix} u_1(\tau) \\ v_1(\tau) \end{pmatrix} + o(s).}$$

$$F_\delta(\bar{z} + h) - A(\bar{z}) h = \begin{pmatrix} -\bar{x} + h_1 + \delta(1 - \bar{x} - h_1) e^{\frac{\delta(\bar{y} + h_2)}{\delta + \bar{y} + h_2}} \\ p\bar{y}_1 - (1+p)(\bar{y} + h_2) + \delta(1 - \bar{x} - h_1) e^{\frac{\delta(\bar{y} + h_2)}{\delta + \bar{y} + h_2}} \end{pmatrix} - \begin{pmatrix} \frac{-h_1}{1 - \bar{x}} + \frac{\delta^2}{(\delta + \bar{y})^2} \bar{x} h_2 \\ \frac{-2\bar{x}h_1}{1 - \bar{x}} - (1+p)h_2 + \frac{d\delta^2\bar{x}h_2}{(\delta + \bar{y})^2} \end{pmatrix}$$

but  $e^{\frac{\delta(\bar{y} + h_2)}{\delta + \bar{y} + h_2}}$  may be expanded and simplified to yield

$$e^{\frac{\delta(\bar{y} + h_2)}{\delta + \bar{y} + h_2}} = \frac{\bar{x}}{\delta(1 - \bar{x})} \left[ 1 + h_2 D + h_2^2 E + h_2^3 F + o(h_2^3) \right]$$

where  $D = \delta^2 / (\delta + \bar{y})^2$  4.4.11

$$E = (\delta^4 - 2\delta^2(\delta + \bar{y})) / 2(\delta + \bar{y})^4. \quad 4.4.12$$

$$F = (\delta^6 - 6\delta^4(\delta + \bar{y}) + 6\delta^2(\delta + \bar{y})^2) / 6(\delta + \bar{y})^6. \quad 4.4.13$$

Therefore;

$$F_\delta(\bar{z} + h) - A(\bar{z}) \cdot h = \left( \bar{x} E h_2^2 \frac{-\bar{x}}{1 - \bar{x}} D h_1 h_2 \begin{pmatrix} 1 \\ d \end{pmatrix} + \left( \bar{x} F h_2^3 \frac{-\bar{x}}{1 - \bar{x}} E h_1 h_2 \begin{pmatrix} 1 \\ d \end{pmatrix} + o(h^3) \right) \right)$$



Consequently

$$\begin{aligned} Q^3(w(\tau, s)) &= \left( \bar{x} E v^2(\tau, s) - \frac{\bar{x}}{1-\bar{x}} D w(\tau, s) v(\tau, s) + s \bar{x} F v^3(\tau, s) - \frac{s \bar{x}}{1-\bar{x}} E v(\tau, s) v(\tau, s) \right) \begin{pmatrix} 1 \\ d \end{pmatrix} + o(s) \\ &= \begin{pmatrix} 1 \\ d \end{pmatrix} \left( \bar{x} E (v^2 + 2s v \cdot v_1) - \frac{\bar{x}}{1-\bar{x}} D (v v + s v v_1 + s v v_1) + s \bar{x} F v^3 - \frac{s \bar{x}}{1-\bar{x}} E v v^2 \right) + o(s) \end{aligned}$$

and differentiation gives;

$$\left. \frac{d}{ds} Q^{(1)}(w(\tau, s)) \right|_{s=0} = \begin{pmatrix} 1 \\ d \end{pmatrix} \left( 2 \bar{x} E v v_1 - \frac{\bar{x}}{1-\bar{x}} D (v v_1 + v v_1) + \bar{x} F v^3 - \frac{\bar{x}}{1-\bar{x}} E v v^2 \right) \quad 4.4.14$$

From the preceding equation one now needs to determine the vectors  $W = \begin{pmatrix} u \\ v \end{pmatrix}$  and  $W_1 = \begin{pmatrix} u_1 \\ v_1 \end{pmatrix}$  as described in proposition 4.3.1

$$W = \begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} \cos w\tau - \frac{\sin w\tau}{w(1-\bar{x})} \\ -\frac{d\bar{x}}{1-\bar{x}} \frac{\sin w\tau}{w} \end{pmatrix} \quad \begin{array}{l} \text{Fundamental} \\ \text{matrix} \\ \text{solution.} \end{array} \quad 4.4.15$$

$$\text{and } W_1 = \begin{pmatrix} u_1 \\ v_1 \end{pmatrix} = \int_0^\tau dq e^{(\tau-q)A^0} \left\{ \bar{x} E v^2 - \frac{\bar{x}}{1-\bar{x}} D v v \right\} \begin{pmatrix} 1 \\ d \end{pmatrix} \quad 4.4.16$$

Noting that  $A \begin{pmatrix} 1 \\ d \end{pmatrix} = \begin{pmatrix} \beta+1 \\ d \end{pmatrix}$  then,

$$W_1(\tau) = \int_0^\tau dq \left\{ \bar{x} E v^2(q) - \frac{\bar{x}}{1-\bar{x}} D v(q) v(q) \right\} \left\{ \begin{pmatrix} 1 \\ d \end{pmatrix} \cos w(\tau-q) + \begin{pmatrix} \beta+1 \\ d \end{pmatrix} \frac{\sin w(\tau-q)}{w} \right\}.$$

Thus

$$W_1(\tau) = \int_0^\tau dq \left\{ \left( 2d \bar{x} E - \frac{2D}{1-\bar{x}} \right) \frac{\sin^2 w\tau}{w} + 2D \sin w\tau \cos w\tau \right\} \begin{pmatrix} \cos w(\tau-q) + \frac{\beta+1}{w} \sin w(\tau-q) \\ d \cos w(\tau-q) + \frac{d}{w} \sin w(\tau-q) \end{pmatrix} \frac{d\bar{x}}{2w(1-\bar{x})^2}$$

and  $\left. \frac{d}{ds} Q^{(s)}(w(\tau, s)) \right|_{s=0}$  may be evaluated as the function overleaf.

$$\begin{aligned}
& \left( \frac{1}{d} \right) \left[ \frac{d\bar{x}}{2w(1-\bar{x})} \left( \left( \frac{-2d\bar{x}}{w(1-\bar{x})} E + \frac{\bar{x}D}{w(1-\bar{x})} \right) \sin w\tau - \frac{\bar{x}D}{1-\bar{x}} \cos w\tau \right) \int_0^\tau [G(w,\tau)] \left\{ d \cos w(\tau-q) + \frac{d}{w} \sin w(\tau-q) \right\} dq \right. \\
& \quad \left. - \frac{d\bar{x}^2}{2w(1-\bar{x})^2} \frac{\bar{x}}{1-\bar{x}} D \left( \frac{-2d\bar{x}}{w(1-\bar{x})} \sin w\tau \right) \int_0^\tau [G(w,\tau)] \left\{ \cos w(\tau-q) + \frac{\beta+1}{w} \sin w(\tau-q) \right\} dq \right. \\
& \quad \left. + \left( \frac{\bar{x}}{1-\bar{x}} E \frac{d^2\bar{x}^2}{w(1-\bar{x})^3} - \frac{\bar{x}F d^2\bar{x}^3}{w^2(1-\bar{x})^3} \right) \sin^3 w\tau - \frac{\bar{x}}{1-\bar{x}} \frac{E d^2\bar{x}^2}{w^2(1-\bar{x})^2} \sin^2 w\tau \cos w\tau \right]
\end{aligned}$$

$$\text{where } G(w,\tau) = \left\{ \left( 2d\bar{x}E - \frac{2D}{1-\bar{x}} \right) \frac{\sin^2 w\tau}{w} + 2D \sin w\tau \cos w\tau \right\}$$

$$\begin{aligned}
\text{Recalling that } e^{-\tau A} \cdot \begin{pmatrix} 1 \\ d \end{pmatrix} &= \left( \cos w\tau \mathbf{I} - \frac{\sin w\tau}{w} A \right) \begin{pmatrix} 1 \\ d \end{pmatrix} \\
&= \cos w\tau \begin{pmatrix} 1 \\ d \end{pmatrix} - \frac{\sin w\tau}{w} \begin{pmatrix} \beta+1 \\ d \end{pmatrix}
\end{aligned}$$

$$\text{then } \int_0^\tau e^{-\tau A} \frac{d}{ds} (Q^s(w(\tau,s))) \Big| \quad \text{becomes a very lengthy}$$

integral of combinations of sine and cosine functions which may be reduced to the following expression after it has been multiplied by the scalar  $\begin{pmatrix} -d\bar{x} \\ 1 \end{pmatrix}$  to eliminate the  $\nabla'(0)$  term as was previously explained.

$$\begin{aligned}
& \left( \int_0^\tau e^{-\tau A} \frac{d}{ds} (Q^s(w(\tau,s))) \Big|_{s=0} d\tau \right) \begin{pmatrix} -d\bar{x} \\ 1 \end{pmatrix} \\
&= \frac{2\pi d^2 \bar{x}^3}{48 w^5 (1-\bar{x})^2} \left[ \left( 2d\bar{x}E - \frac{2D}{1-\bar{x}} \right) \left\{ -2 \left( -2d\bar{x}E + \frac{D}{1-\bar{x}} \right) - 7D - \frac{2\bar{x}D}{1-\bar{x}} + 5 \left( -2d\bar{x}E + \frac{D}{1-\bar{x}} \right) \right. \right. \\
& \quad \left. \left. + 2Dw^2 + 5(\beta+1) \frac{\bar{x}}{1-\bar{x}} D \right\} + \left( -2d\bar{x}E + \frac{D}{1-\bar{x}} \right) (-2D + 4Dw^2) \right. \\
& \quad \left. + 2D^2 \left\{ 2w^2 - \frac{(\beta+1)\bar{x}}{1-\bar{x}} + w^2 + \frac{2\bar{x}w^2}{1-\bar{x}} \right\} + 6Ew^2 \left( \frac{3}{1-\bar{x}} - 1 \right) - 18dw^2 \bar{x}F \right]
\end{aligned}$$

$$= \frac{2\pi \cdot d^3 \bar{x}^3}{48w^5(1-\bar{x})^2} \left\{ -3 \left( 2d\bar{x}E - \frac{2D}{1-\bar{x}} \right)^2 - 3D(1-w^2) \left( 2d\bar{x}E - \frac{2D}{1-\bar{x}} \right) - 6w^2 \left( -\frac{E\bar{x}+2}{1-\bar{x}} + 3d\bar{x}F \right) \right\}$$

Resubstitution of this formula and the result of the expression for  $\left( \left( C^0 - \frac{1}{w^2} A^0 C^0 A^0 \right) \begin{pmatrix} 1 \\ 0 \end{pmatrix} \right) \cdot \begin{pmatrix} -da \\ 1 \end{pmatrix}$  back into

the original bifurcation equation as described by equation 4.3.11 yields an expression for the  $[\Delta'(0)]$  function for "finite  $\delta$ "

$$\Delta'(0) = \frac{-d^2 a^2 b^2}{8w^4 \text{Tr} C^0} \left\{ [2daE - 2Db]^2 + D[2daE - 2Db] + D^2 [6daf - 2E(a+2)b + 2daDE + 2b^2] \right\} \quad 4.4.18$$

Initially, one could evaluate this function for  $\delta = \infty$  (infinite).

$$\begin{aligned} \text{In this case} \quad D_c &\rightarrow 1 \\ E_c &\rightarrow 1/2 \\ F_c &\rightarrow 1/6 \end{aligned} \quad 4.4.19$$

$$\text{and } \Delta'(0) = \frac{d^2 a^2 b^2}{8w_0^4 \text{Tr} C^0} \cdot \left\{ w_0^2(b-1) + (2b-da) - (2b-da)^2 \right\} \quad 4.4.20$$

$$\begin{aligned} \text{where } D &= dS_i - 1 - \beta \quad \text{for } i = 1 \text{ or } 2 \\ a &= S_i \\ \text{and } w^2 &= da^2b - b^2 \end{aligned}$$

This expression is in agreement with the result as obtained by Poore<sup>11)</sup>

Comment:- In the infinite case, once  $d$  and  $\beta$  are given then the sign of  $\Delta'(0)$  is known. In the finite case, evaluation of  $\bar{x}$  and  $\bar{y}$  is achieved through numerical iterative procedures leading to a far more complicated routine in ascertaining the sign of  $\Delta'(0)$  at criticality.

## CHAPTER FIVE

### 5 NUMERICAL ANALYSIS

#### 5.1 ABOUT NAG

Now that the modelling and the associated analytical work has been duly carried out for this two dimensional non-linear system it is wholly appropriate to confirm the analysis by carrying out further detailed numerical work.

The numerical algorithms group (N.A.G.) Fortran library is very extensive and the Mark 11 revised routines were used to solve this system of ordinary differential equations.

The NAG library offers a range of "Driver" programmes which may be suitably altered for the programmers needs. In the NAG Fortran library, the author chose routine D02EBF which integrates a STIFF system of first order ordinary differential equations over a range with suitable initial conditions using a variable-order variable-step GEAR method, and returns a solution at points specified by the user.

Indeed to give the reader an appreciation of the extent of the library for ordinary differential equations alone, a summary of available routines are copied overleaf in Table 5.1 1.

A special class of initial-value problems are those for which the solutions contain rapidly decaying transient terms. Such problems are called stiff: an alternative way of describing them is to say that certain eigenvalues of the Jacobian matrix  $\frac{\partial f_i}{\partial y_j}$  have large negative real parts when compared to others. These problems require special methods for efficient numerical solution: the methods designed for non-stiff problems tend to be very slow, because they need small step-lengths to avoid numerical instability

# SUMMARY OF AVAILABLE ROUTINES

| Problem                                                             | Routine        |        |               |
|---------------------------------------------------------------------|----------------|--------|---------------|
|                                                                     | Merson's       | Adams  | Gears         |
| INITIAL-VALUE PROBLEMS                                              |                |        |               |
| Driver Routines ... ..                                              |                |        |               |
| Integration over a range                                            | D02BAF         | D02CAF | D02EAF        |
| - with intermediate output                                          | D02BBF         | D02CBF | <u>D02EBF</u> |
| - with global error estimate and stiffness check                    | D02BDF         | -      | -             |
| Integration until a component of the solution attains a given value | D02BGF         | D02CGF | D02EGF        |
| Integration Routines                                                | D02PAF         | D02QAF | D02QBF        |
| Integration over one step                                           | D02YAF         | -      | -             |
| Interpolation on the solution                                       |                |        |               |
| all components                                                      | D02XAF         | D02XGF | D02XGF        |
| one component                                                       | D02XBF         | D02XHF | D02XHF        |
| BOUNDARY-VALUE PROBLEMS                                             |                |        |               |
| Shooting Method .. ...                                              |                |        |               |
| simple parameters                                                   | D02HAF         |        |               |
| generalised parameters                                              | D02HBF, D02AGF |        |               |
| additional facilities                                               | D02SAF         |        |               |
| Finite difference method ..                                         |                |        |               |
| simple parameters                                                   | D02GAF         |        |               |
| linear problem                                                      | D02GBF         |        |               |
| full non-linear problem                                             | D02RAF         |        |               |
| Chebyshev collocation . ...                                         |                |        |               |
| single equation                                                     | D02JAF         |        |               |
| first order system                                                  | D02JBF         |        |               |
| general system                                                      | D02TGF         |        |               |
| Sturm-Liouville Eigenvalue ...                                      |                |        |               |
| regular problems                                                    | D02KAF         |        |               |
| general problems                                                    | D02KDF         |        |               |
| eigenfunction calculation                                           | D02KEF         |        |               |

Table 5.1.1

To solve the equations arising in Gears method an approximation to the Jacobian matrix  $\frac{\partial f}{\partial y}$  is required. This approximation can be calculated internally, but the user may supply an analytical expression for the Jacobian via a parameter to the routines D02EBF, D02EHF and D02QBF. In most cases supplying a correct analytical expression will reduce the amount of computer time used.

The elementary driver programme, which itself "calls up" the appropriate NAG programme, has been extensively modified by the author.

A process flow chart is given overleaf for clarity.

In this case, the routine integrates a system of ordinary differential equations

$$Y_i = F_i(T, Y_1, Y_2) \quad i = 1, 2 \quad 5.2.1$$

from  $T = X$  to  $T = X_{\text{end}}$ . The system is defined by subroutine FCN which evaluates  $F_i$  in terms of  $T$ , and  $Y_1$ ,  $Y_2$ . The solution is returned via the user supplied routine OUTPUT at a specified set of points. The accuracy of the integration and the interpolation is controlled by the parameters TOL and IRELAB. The Jacobian of the system  $Y' = F(T, Y)$  is supplied in the routine PEDERV.

Further details on the programme specifications, error warnings, and other parameters may be obtained in the D02EBF-NAG Fortran library routine document

A copy of the modified programme is attached. Each section's function is clearly described in the programme and may be followed by using the complimentary flow chart.

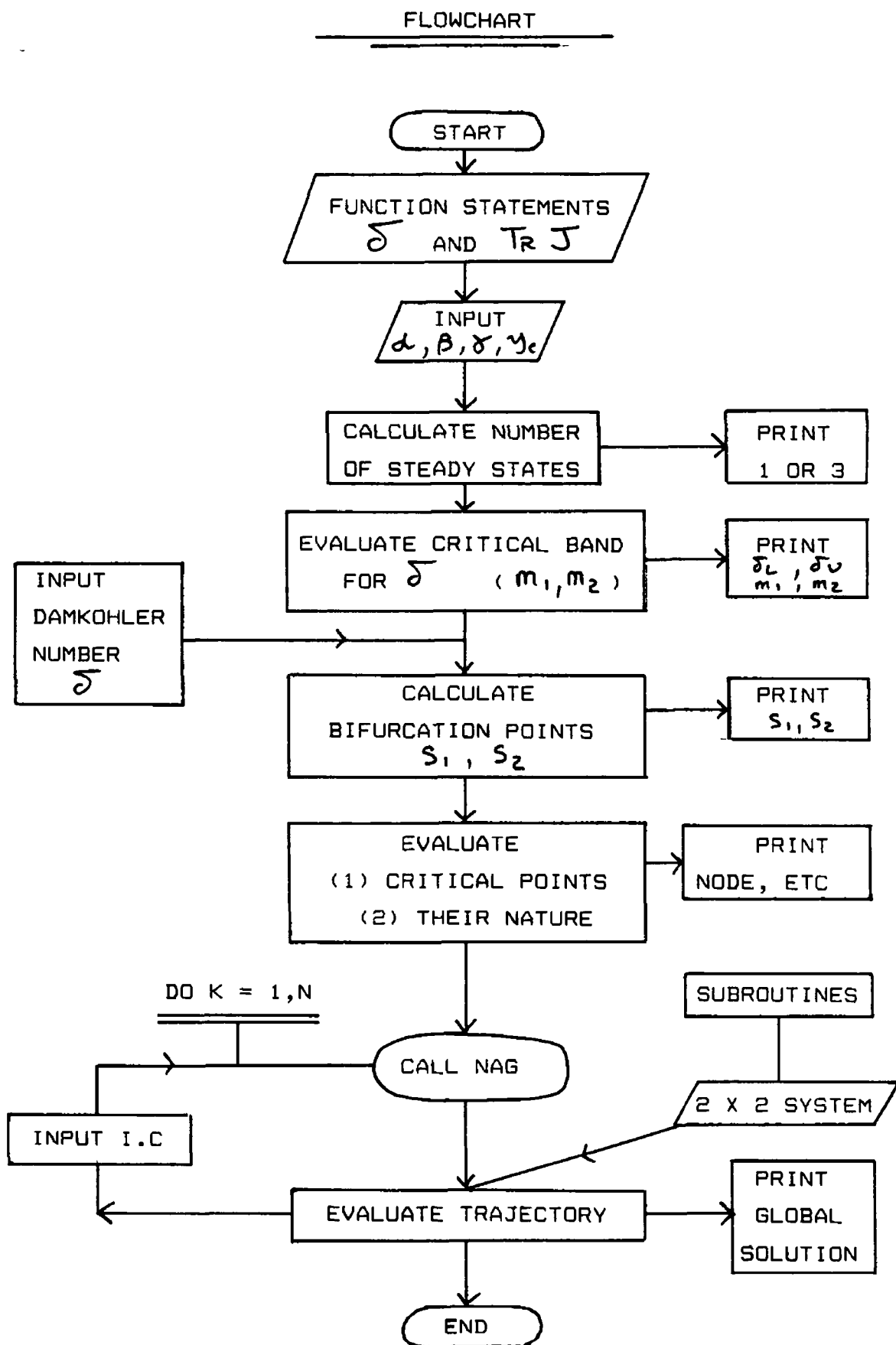


Figure 5 2.1



```

C      - - CONTINUOUS STIRRED TANK REACTOR (C.S.T.R.) - MODEL
C
C      (A)      THE DAMKOHLER FUNCTION
C
C              FUNCTION UU (G,S,TT)
C              REAL*8 UU, G,S,TT
C              UU = S - ( G / ( 1.000 - G ) ) * DEXP ( TT )
C              RETURN
C              END
C
C      FUNCTION BB(G,P,Q,R,U,TT,V)
C      REAL*8 BB,G,P,Q,R,U,TT,V
C              BB = ((( ( P/R ) ** 2.000 + P * ( 1.000 + Q ) ) * ( G * G ) )
1      + ( ( ( V * 2.000 ) * ( P/R ) - P * ( 1.000 + Q ) ) * G ) + ( V * V ) ) *
2      ( - DEXP ( TT ) ) / ( ( ( 1.000 - G ) * ( V + ( P * G / R ) ) ) ** 2.000 )
C      RETURN
C      END
C
C      (B)      THE TRACE OF THE LINEARISED SYSTEM
C
C      FUNCTION CC(X,Y,P,Q,R)
C      REAL*8 CC,X,Y,P,Q,R,
C              CC = -1.000 / ( 1.000 - X ) - ( 1.000 + Q ) + (
1      P * X ) / ( ( 1.000 + ( Y / R ) ) ** 2.000 )
C      RETURN
C      END
C
C      FUNCTION HH(X,Y,P,Q,R)
C      REAL*8 HH,X,Y,P,Q,R
C              HH = ( -1.000 / ( ( 1.000 - X ) ** 2.000 ) ) + P / ( (
1      1.000 + ( Y / R ) ) ** 2.000 ( - ( 2.000 * P * P * X ) / ( ( 1.000 + Q
2      ) * R * ( ( 1.000 + ( Y / R ) ) ** 3.000 ) )
C      RETURN
C      END
C
C      INPUTTING ALPHA (P), BETA (Q), GAMMA (R), Yc (U)
C
C      SUBROUTINE CONST(P,Q,R,U,)
C      REAL*8 P,Q,R,U
C      P = 8.000
C      Q = 3.000
C      R = 20.000
C      U = -2.000
C      RETURN
C      END
C
C      IMPLICIT REAL*8 (A-H,O-Z)
C      REAL*8 XEND, TOL
C      INTEGER I, IFAIL, IR, IW, J, MPED, N, NOUT, ITER, ITMAX
C      REAL*8 W(2,20), Y(2)
C      EXTERNAL FCN, OUT, PEDERV
C      COMMON /SFACT/S, XEND, H, I, TOL, A, B, NOUT

```

```

C      -----
C      (1)      CALCULATING THE NUMBER OF STEADY STATES
C
      CALLCONST(P,Q,R,U)
      V = (1.000 + Q + (Q*U/R))
      Z = (4*(V**2))/((1.000 + Q) - (4/R)*V)
      WRITE ( 6,1040 )
      READ(5,1050)NQUT
      WRITE(NQUT,1090)
      WRITE(NQUT,1060)Z
      IF ( P - Z )1010,1010,1020
1010  WRITE(NQUT,1080)
      GO TO 1030
1020  WRITE(NQUT,1070)
1030  CONTINUE
C
1040  FORMAT(," INPUT THE OUTPUT CHANNEL ")
1050  FORMAT( I1 )
1060  FORMAT(40HOMULTIPLE STEADY STATES REQUIRES ALPHA>, F10.4)
1070  FORMAT(/,10X," ** THREE CRITICAL POINTS MAY EXIST ** ",/)
1080  FORMAT(/,10X," ** ONLY ONE CRITICAL POINT EXISTS ** ",/)
1090  FORMAT(4(1X/), 31H D02EBF EXAMPLE PROGRAM RESULTS/1X)
C
C      (2)      EVALUATING THE CRITICAL RANGE
C                  FOR THE DAMKOHLEK NUMBER
C
      Q1 = ( 1.000 + Q )
      B1 = ((( P/R )**2 000 ) + ( Q1*P))
      DM3 = ( P*P )*(( ( 2 000*Q*U)/( R*R ) ) + (( 2 000/R ( -
1      1.000*Q1**2 000 ) - ( 4 000*V*V*B1)
      IF (DM3 LT.0 0) GO TO 2030
      DM2 = (( -P*(( ( 2 000/R )*V )- Q1 )) + (( DM3 )**0.5000
1      ))/( 2*B1 )
      DM1 = (( -P*(( ( 2 000/R )*V )- Q1 )) - (( DM3 )**0.5000
1      ))/( 2*B1 )
      TM1 = ( - ( P*DM1 +Q*U )/( V + (( P*DM1 )/R )))
      DK1 = ( DM1/( 1.000 - DM1 ))*DEXP( TM1 )
      TM2 = ( - ( P*DM2 +Q*U )/( V + (( P*DM2 )/R )))
      DK2 = ( DM2/( 1.000 - DM2 ))*DEXP( TM2 )
      WRITE(NQUT,2010)DK2,DM2
      WRITE(NQUT,2020)DK1,DM1
C
2010  FORMAT (/,3X," THE LOWER CRITICAL DAMKOHLEK VALUE IS " ,
1      D12.6," AT X = ",D12.6,// )
2020  FORMAT (/,3X," THE UPPER CRITICAL DAMKOHLEK VALUE IS " ,
1      D12.6, " AT X = ",D12.6,// )
2030  CONTINUE
C

```

```

C
C      (3)      PERIODIC BIFURCATION
C
      CALL CONST(P,Q,R,U)
      ITMAX = 20
      EPS = 1.0D-10
      DO3040 L =2,1000
          X = 0.0010D0*( L -1 )
          ITER = 0
          DIFF = 1.0D0
          Y0 = ( P*X + Q*U )/( 1.0D0 + Q )
          FTRX = CC(X,Y0,P,Q,R)
          XN = ( X - 0.0010D0 )
          YN = ( P*XN + Q*U )/( 1.0D0 + Q )
          FTRN = CC(XN,YN,P,Q,R)
          IF ( FTRN .EQ. 0.0D0 )GO TO 3050
          IF ( FTRX/FTRN ) 3010,3010,3040
3010      DO WHILE ((DIFF.GT EPS).AND.(ITER.LT.ITMAX))
          ITER = ITER + 1
          Y0 = ( P*X + Q*U )/( 1.0D0 + Q )
          FTRX = CC(X,Y0,P,Q,R)
          ATRX = HH(X,Y0,P,Q,R)
          X1 = X - ( FTRX/ATRX )
          DIFF = DABS( X1 - X )
          X = X1
          END DO
3050      CONTINUE
      DEL = ( X/( 1.0D0 - X ))*DEXP( -Y0/( 1.0D0 + ( Y0/R )))
      WRITE(NOUT,3030)X1,DEL
3030      FORMAT(/,3X," PERIODIC BIFURCATION AT X = "D12.6," AND A
1      DAMKOHLEH CONSTANT OF ",D12.6 )
3040      CONTINUE
C

```

```

C      (4)      EVALUATING THE CRITICAL POINTS AND THEIR NATURE
C      --
C      WRITE(6,4030)
C      READ(5,4040)S
C      WRITE(NOUT,4050)S
C      ITMAX = 20
C      EPS = 1.0D-9
C      WRITE(NOUT,4020)
C
C      DO 4150 K =2,1000
C          G = 0.0010D0*( K - 1 )
C          ITER = 0
C          DIFF = 1.0D0
C          TT = ( - ( P*G + Q*U )/( V + ( P*G/R ) ) )
C          FF = UU(G,S,TT)
C          GP = ( G - 0.0010D0 )
C          TP = ( - ( P*GP + Q*U )/( V + ( P*GP/R ) ) )
C          FP = UU(GP,S,TP)
C          IF ( FF/FP ) 4010,4010,4150
4010      DO WHILE ((DIFF.GT.EPS).AND (ITER.LT.ITMAX))
C          TT = ( - ( P*G + Q*U )/( V + ( P*G/R ) ) )
C          ITER = ITER + 1
C          FF = UU(G,S,TT)
C          FA = BB,G,P,Q,R,U,TT,V)
C          G1 = G - FF/FA
C          DIFF = DABS( G1 - G )
C          IF (DIFF.GT.1.0D0)GO TO 4150
C          G = G1
C          END DO
C
C      G2 = ( P*G + Q*U )/( 1.0D0 + Q )
C      TRJ = ( - 1.0D0/( 1.0D0 - G ) ) - ( 1.0D0 + Q ) + (( P*G)/
1      (( 1.0D0 + ( G2/R ) )**2.0D0 ) )
C      DETJ = ( 1.0D0 + Q )/( 1.0D0 - G ) - (( P*G )/
1      (( 1.0D0 + ( G2/R ) )**2.0D0 ) )
C      DELJ = (( TRJ**2.0D0 ) - ( 4.0D0*DEJ ) )
C      WRITE(NOUT,4130)
C      WRITE(NOUT,4120)TRJ,DEJ,DELJ
C      WRITE(NOUT,4140)G,G2
C      IF( DEJ.LT.0.0 )WRITE(NOUT,4060)
C      IF(DEJ.GT.0.0.AND.DELJ.GT.0.0.AND.TRJ.LT.0.0)WRITE(NOUT,4070)
C      IF(DEJ.GT.0.0.AND.DELJ.GT.0.0.AND.TRJ.GT.0.0)WRITE(NOUT,4080)
C      IF(DEJ.GT.0.0.AND.DELJ.LT.0.0.AND.TRJ.EQ.0.0)WRITE(NOUT,4090)
C      IF(DEJ.GT.0.0.AND.DELJ.LT.0.0.AND.TRJ.GT.0.0)WRITE(NOUT,4100)
C      IF(DEJ.GT.0.0.AND.DELJ.LT.0.0.AND.TRJ.LT.0.0)WRITE(NOUT,4110)
4020  FORMAT(/,20X,"*****",/,20X,
1      "* EVALUATING THE CRITICAL POINTS *",/,20X,"*",8X,
2      "AND THEIR NATURE",8X,"",/,20X,
3      "*****"//)
4030  FORMAT( " INPUT THE DAMKOHLER NUMBER " )
4040  FORMAT(D12.6)
4050  FORMAT(/,3X,"THE DAMKOHLER CONSTANT IS",D12.6,/)
4060  FORMAT(/,3X," THIS CRITICAL POINT IS A SADDLE POINT ",//)
4070  FORMAT(/,3X," THIS CRITICAL POINT IS A STABLE NODE ",//)
4080  FORMAT(/,3X," THIS CRITICAL POINT IS AN UNSTABLE NODE ",//)

```

```

4090  FORMAT(/.3X," THIS CRITICAL POINT IS A CENTRE ",//)
4100  FORMAT(/.3X," THIS CRITICAL POINT IS AN UNSTABLE SPIRAL ",//)
4110  FORMAT(/ 3X," THIS CRITICAL POINT IS A STABLE SPIRAL ",//)
4120  FORMAT(/,3X,3(3X,D13.6))
4130  FORMAT/,8X," TRACE J  ",3X,"DETERMINANT J",3X," DELTA J" )
4140  FORMAT(/5X,"A STEADY STATE IS X = ",D12.6,2X,"Y = ",D12.6,/,
4150  CONTINUE
C
C      (6)      EVALUATING TRAJECTORIES BY GEARS METHOD
C                  FOR VARIOUS INITIAL CONDITIONS
C
      WRITE(NOUT,6140)
      N = 2
      IW = 20
      MPED = 0
      A = 0.0D0
      B = 0.0D0
      IR = 2
      DO 6020 K = 1,1
      WRITE(6,6030)
      READ(5,6060)Y(1),Y(2)
      WRITE(NOUT,6040) Y(1),Y(2)
      DO 6010 J = 5,5
      TOL = 10.**(-J)
      WRITE(NOUT,6090) TOL
      WRITE(NOUT,6050) S
      WRITE(NOUT,6100)
      X = 0.0D0
      XEND = 20.0D0
      H = (XEND - X)/400.0D0
      I = 399
      IFAIL = 1
      CALL D02EBF(X,XEND,N,Y,TOL,IR,FCN,MPED,PEDERV,
1      OUT,W,IW,IFAIL)
      WRITE(NOUT,6110)IFAIL
      IF (TOL.LT 0.0)WRITE(NOUT,6130
6010  CONTINUE
6020  CONTINUE
C
      MPED = 1
      WRITE(NOUT,6150)
      DO 6080 K = 1,1
      WRITE(6,6030)
      READ(5,6060)Y(1),Y(2)
      WRITE(NOUT,6040)Y(1),Y(2)
      DO 6070 J = 5,5
      TOL = 10.**(-J)
      WRITE(NOUT,6090)TOL
      WRITE(NOUT,6050)S
      WRITE(NOUT,6100)
      X = 0.0D0
      XEND = 20.0D0
      H = (XEND - X)/20.0D0
      I = 19
      IFAIL = 1

```

```

      CALL D02EBF(X,XEND,N,Y,TOL,IR,FCN,MPED,PEDERV,
1      OUT,W,IW,IFAIL)
      WRITE(NOUT,6110)IFAIL
      IF (TOL.LT.0.) WRITE(NOUT,6130)
6030  FORMAT( " INPUT INITIAL CONDITIONS ")
6040  FORMAT(/,3X, "INITIAL CONDITIONS ARE Y(1)
1      = ",D12.6," Y(2) = ",D12.6 )
6050  FORMAT (/,3X, " DAMKOHLER CONSTANT = ",F10.4,// )
6060  FORAMT( 12D12.6 )
6070  CONTINUE
6080  CONTINUE
6090  FORMAT(22HOCALCULATION WITH TOL = , D8.1 )
6100  FORMAT(40H X AND SOLUTION AT EQUALLY SPACED POINTS)
6110  FORMAT(8H IFAIL = , I1)
6130  FORMAT(24H RANGE TOO SHORT FOR TOL)
6140  FORMAT(32HOCALCULATING JACOBIAN INTERNALLY)
6150  FORMAT(31HOCALCULATING JACOBIAN BY PEDERV)
      STOP
      END

```

```

C
C      THE (2*2) C.S T R. SYSTEM MODEL
C
C      SUBROUTINE FCN(T,Y,F)
      REAL*8 T
      REAL*8 F(2),Y(2)
      COMMON/SFACT/S,XEND,H,T,TOL,A,B,NOUT
      CALL CONST(P,Q,R,U)
      F(1) = -Y(1) + (S*(1.0D0-Y(1))*DEXP((Y(2)))/
1      (1.0D0+((Y(2))/R)))
      F(2) = -Y(2) + (P*S*(1.0D0-Y(1))*DEXP((Y(2)))/
1      (1.0D0+((Y(2))/R))) - Q*((Y(2)) -U )
      RETURN
      END
C

```

```

C      --- THE JACOBIAN MATRIX
C
C      SUBROUTINE PEDERV(X,Y,PW)
      REAL*8 X
      REAL*8 PW(2,2),Y(2)
      COMMON/SFACT/S,XEND,H,I,TOL,A,B,NOUT
      CALL CONST(P,Q,R,U)
      Z = S*DEXP(-Y(2))/(1.0D0 + ((Y(2))/R))
      PW(1,1) = -1.0D0 - Z
      PW(1,2) = ((Y(1) - 1.0D0)*Z)/((1.0D0 + ((Y(2))/R))**2.0D0)
      PW(2,1) = - P*Z
      PW(2,2) = - (1.0D0 + Q) - (P*(1.0D0 - Y(1))*Z)
1      /((1.0D0 + ((Y(2))/R))**2.0D0)
      RETURN
      END

C      PRINTING THE UNIQUE SOLUTION
C
C      SUBROUTINE OUT(X,Y)
      INPLICIT REAL*8 (A-H,O-Z)
      REAL*8 Y(2)
      COMMON/SFACT/S,XEND,H,I,TOL,A,B,NOUT
      INTEGER J, NOUT,I
      CALL CONST (P,Q,R,U)
      WRITE (NOUT,9010) X, (Y(J),J = 1,2)
      WRITE(6,9010) X, (Y(J),J =1,2)
      TT1 = DABS(Y(1)-A)
      TT2 = DABS(Y(2)-B)
      TT3 = DMAX1(TT1,TT2)
      IF (TT3 LT TOL) RETURN
      X = XEND - FLOAT(I)*H
      I = I - 1
      A = Y(1)
      B = Y(2)
      RETURN
9010  FORMAT ( 1H , F7.2 ,2D10.3)
      END

```

## 5.3

CLASSIFICATION OF DYNAMIC BEHAVIOUR  
IN PARAMETRIC SPACE

For fixed  $\alpha$  ,  $\beta$  ,  $\delta$  ,  $\gamma_c$  , the dependence of the steady state conversion  $x$  , and the steady state temperature  $\gamma$  , on the Damkohler number  $\delta$  , is investigated for the system.

$$\begin{aligned}\dot{x} &= -x + \delta(1-x)\exp\left(\frac{\gamma}{1+\gamma/\delta}\right) \\ \dot{\gamma} &= -\gamma + \alpha \delta(1-x)\exp\left(\frac{\gamma}{1+\gamma/\delta}\right) - \beta(\gamma - \gamma_c)\end{aligned}\quad 5.3 \ 1$$

However for various relationships of the parameters  $\alpha$  ,  $\beta$  ,  $\delta$  and  $\gamma_c$  , the dynamic behaviour may be specifically classified as is fully outlined in Chapter Three, Table 3.4.1.

At this point, the range of problems available to the author is infinite.

A significant departure from previous papers on the C.S.T.R. is made in the fact that  $\delta$  will be taken to be finite.

In order to assist an overview of results: typical fixed values will be taken for the following two constants.

$$\begin{aligned}\delta &= \frac{E}{R T_f} = 20 && \text{Arrhenius constant} \\ \gamma_c &= \left(\frac{T_c - T_f}{T_f}\right)\delta = -2 && \text{Cooling constant}\end{aligned}\quad 5.3 \ 2$$

This leads to a representation of the  $(\alpha, \beta)$  parametric space where three lines of criticality may be specified.



These critical lines arise from the following conditions

- |    |     |                                                                                                                                       |                     |
|----|-----|---------------------------------------------------------------------------------------------------------------------------------------|---------------------|
| M  | (1) | $d = \left\{ \frac{4(1+\beta + \frac{\beta y_c}{\delta})^2}{1+\beta - \frac{4}{\delta}(1+\beta + \frac{\beta y_c}{\delta})} \right\}$ | Multiplicity        |
| S  | (2) | $S_1, S_2, \text{ real}$                                                                                                              | Dynamic instability |
| SM | (3) | $S_1 = M_1$                                                                                                                           | Qualitative change  |

Various regions in parametric space are described by these three lines as shown below in Fig. 5.3.1 The interpretation of the nature of the equilibria within these regions is slightly complex as the relative values to one another of the roots  $m_1, m_2, S_1$  and  $S_2$ , needs to be known and whether or not these roots are complex These curves are best solved empirically <sup>13)</sup>

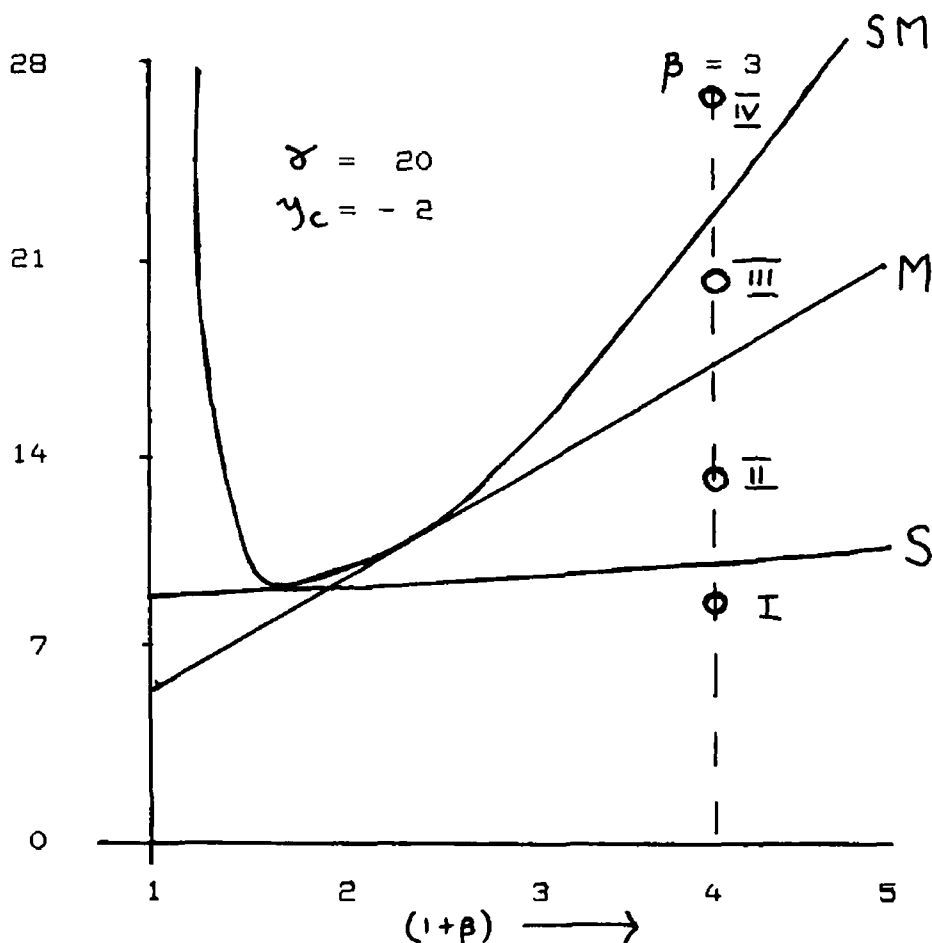


Fig. 5.3.1

The purpose of this chapter is not to rigidly define all possible solution sets to this problem but moreover to present a flavour to the reader of the range of solutions with particular reference to Hopf's Bifurcation phenomena.

In this light therefore, a sample of numerical solutions was obtained for a range of parameters as shown on Fig. 5.3.1

The constants  $\beta$ ,  $\delta$ , and  $\gamma_c$  were fixed as follows

$$\begin{aligned}\beta &= 3 \\ \delta &= 20 \\ \gamma_c &= -2\end{aligned}\quad \text{All typical values.}$$

The dimensionless group number ( $\alpha$ ) was varied as shown in Table 5.4.1 below to give four distinctive points on the ( $\alpha$ ,  $\beta$ ) plane.

| Region | $\alpha$ | Root Sequence                       |
|--------|----------|-------------------------------------|
| I      | 8        | $m_1, m_2, s_1, s_2$ . complex      |
| II     | 12       | $m_1, m_2$ complex, $s_1, s_2$ real |
| III    | 20       | $0 < s_1 < m_1 < m_2 < s_2 < 1$     |
| IV     | 26       | $0 < m_1 < s_1 < m_2 < s_2 < 1$     |

Table 5 4.1

The programme was run for these four cases choosing appropriate values for  $\delta$ , the Damkohler number, and suitable initial conditions. Results from each of the four cases are summarised overleaf in Table 5.4.2.

The Damkohler numbers were chosen, where possible, so that at least one equilibrium lay close to the conversion values  $s_1$  or  $s_2$ . Thus it became possible to numerically see Hopf's bifurcation as is shown in the next section on the analysis of data.

Multiplicity requires  $\alpha > 16.7975$ .

| REGION                          | I         | II        | III                                 | IV                                         |
|---------------------------------|-----------|-----------|-------------------------------------|--------------------------------------------|
| ALPHA ( $\alpha$ )              | 8         | 12        | 20                                  | 26                                         |
| $\delta_1$                      | -         | -         | 0.3708                              | 0.1653                                     |
| $\delta_0$                      | -         | -         | 0.4302                              | 0.3070                                     |
| $\delta$                        | 1.70      | 0.996     | 0.43016                             | 0.2648                                     |
| CRITICAL<br>POINTS              | 1         | 1         | 3                                   | 3                                          |
| $S_1$                           | -         | 0.5000    | 0.2629                              | 0.1974                                     |
| $S_2$                           | -         | 0.7859    | 0.8955                              | 0.9162                                     |
| $m_1$                           | -         | -         | 0.2698                              | 0.7107                                     |
| $m_2$                           | -         | -         | 0.6265                              | 0.1822                                     |
| NATURE OF<br>CRITICAL<br>POINTS | SPIRAL(S) | SPIRAL(S) | SPIRAL(U)<br>SADDLE(U)<br>SPIRAL(U) | SPIRAL(S)<br>SADDLE(U)<br>SPIRAL(U)<br>(*) |

Table 5 4 2

A sample of the programme results for case IV is attached overleaf. All the data under the column marked asterisk (\*) may be found on the programme page.

The "trajectory" data is not given as hundreds of data points are evaluated. However, the resulting graph is given in detail.



As can be seen from the results, the values of the Damkohler number was chosen where possible to evoke periodic orbits as the phase trajectories.

These results may only be understood by examining the following two diagrams for each case.

- (1) Conversion ( $x$ ) versus Damkohler number ( $\delta$ )
- (2) Phase trajectory: ( $y$ ) versus ( $x$ ).

For the four cases shown the following Table summarises the results.

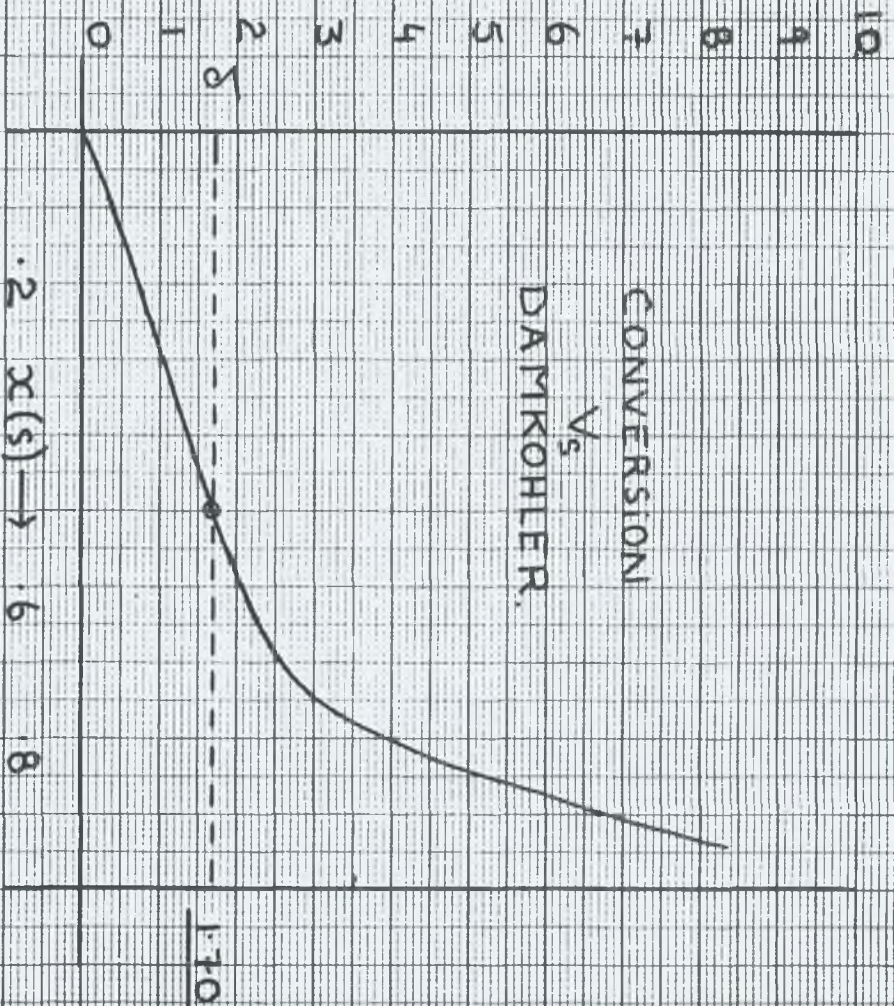
| Case             |          | I | II | III | IV |
|------------------|----------|---|----|-----|----|
| Node             | Stable   | 1 | 1  | 0   | 1  |
| Spiral           | Unstable | 0 | 0  | 2   | 1  |
| Saddle           |          | 0 | 0  | 1   | 1  |
| Limit            | Stable   | 0 | 1  | 1   | 1  |
| Cycle            | Unstable | 0 | 1  | 0   | 0  |
| Total Invariants |          | 1 | 3  | 4   | 4  |

Table 5 4 3



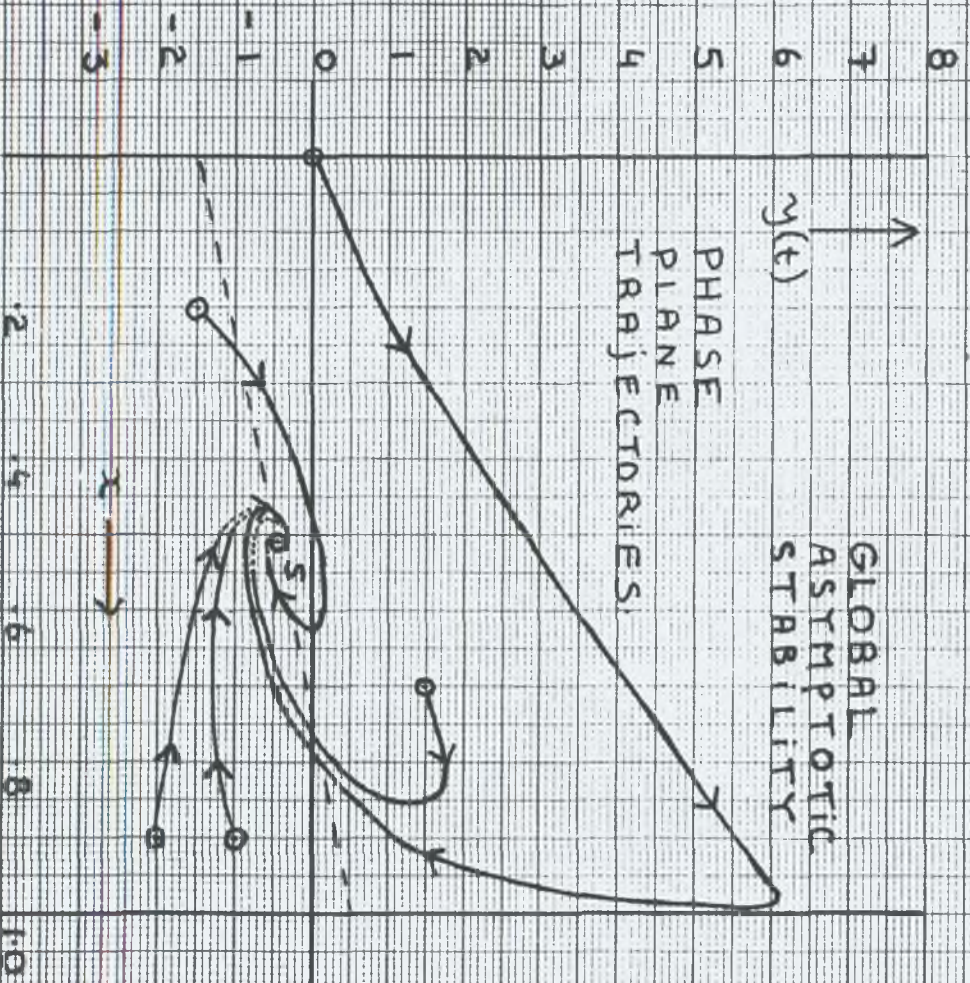
# REGION II

CONVERSION  
 $V_5$   
DAMPKOHLER.



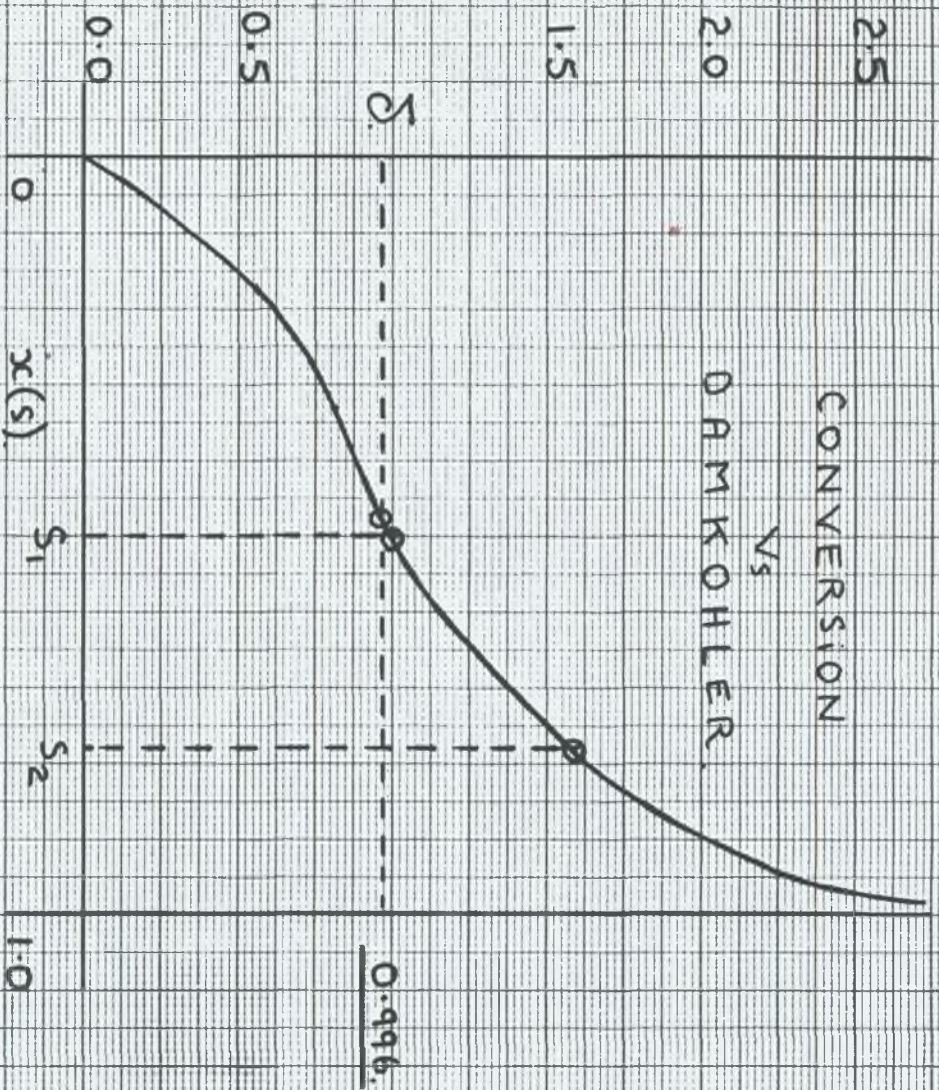
GLOBAL  
ASYMPTOTIC  
STABILITY

PHASE  
PLANE  
TRAJECTORIES

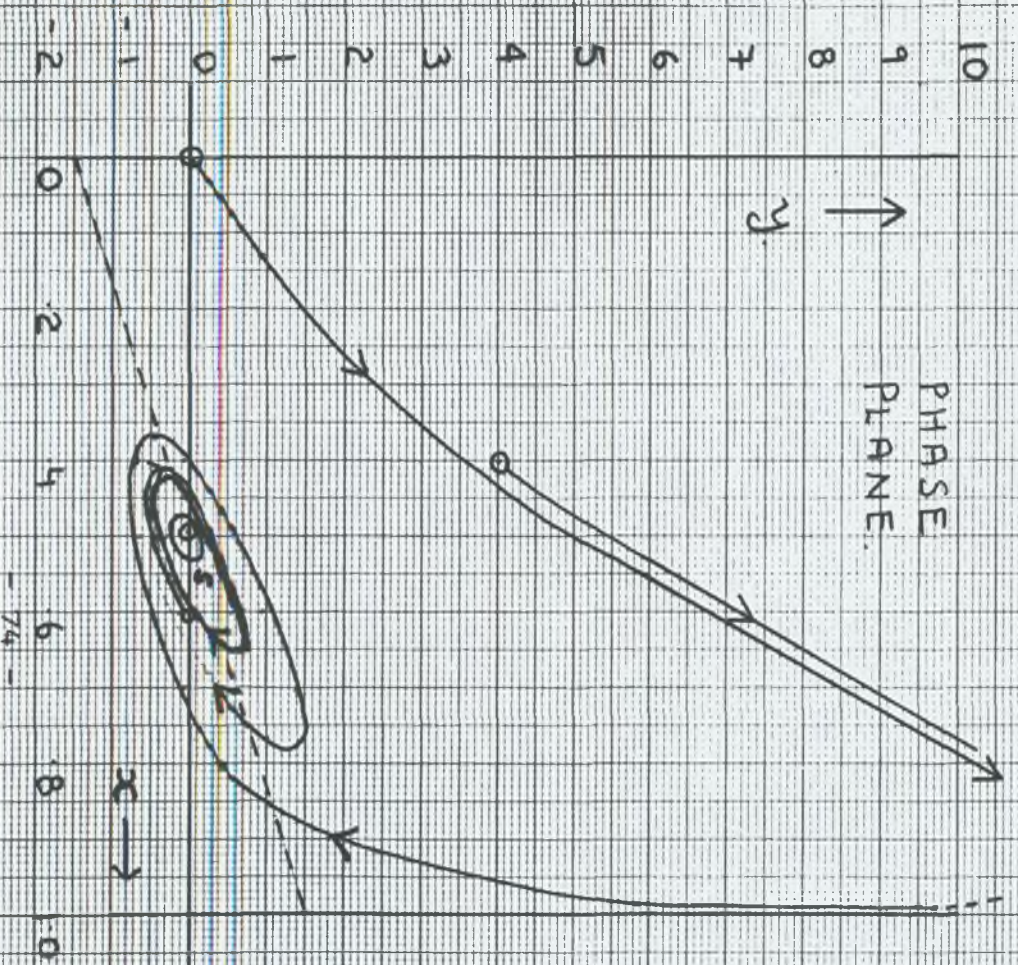




# REGION II

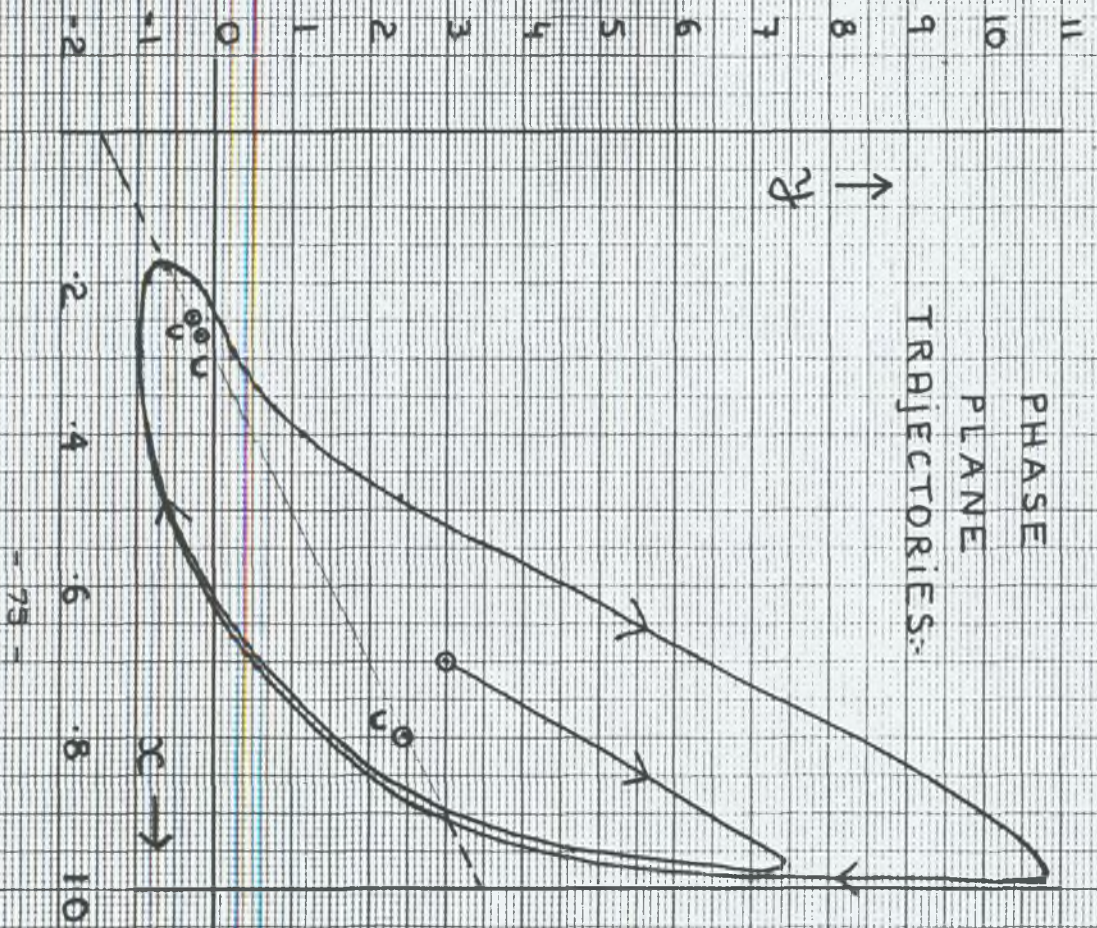
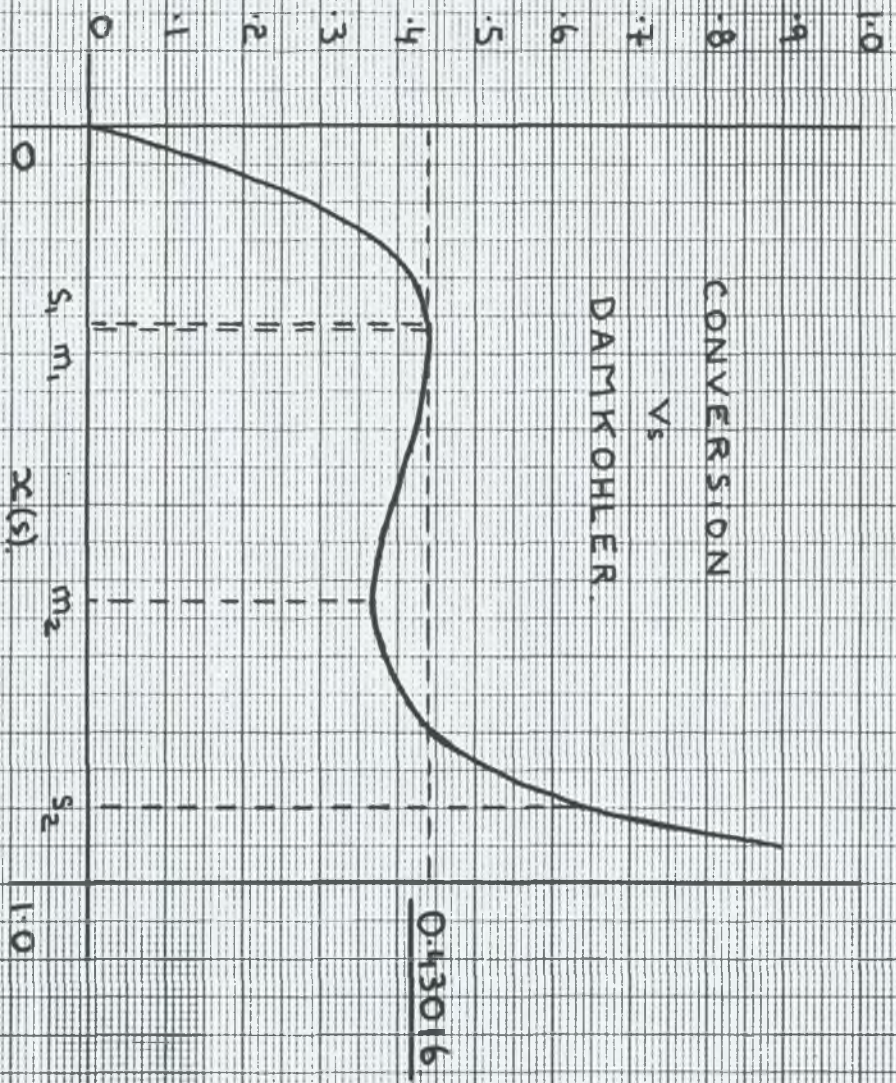


PHASE PLANE



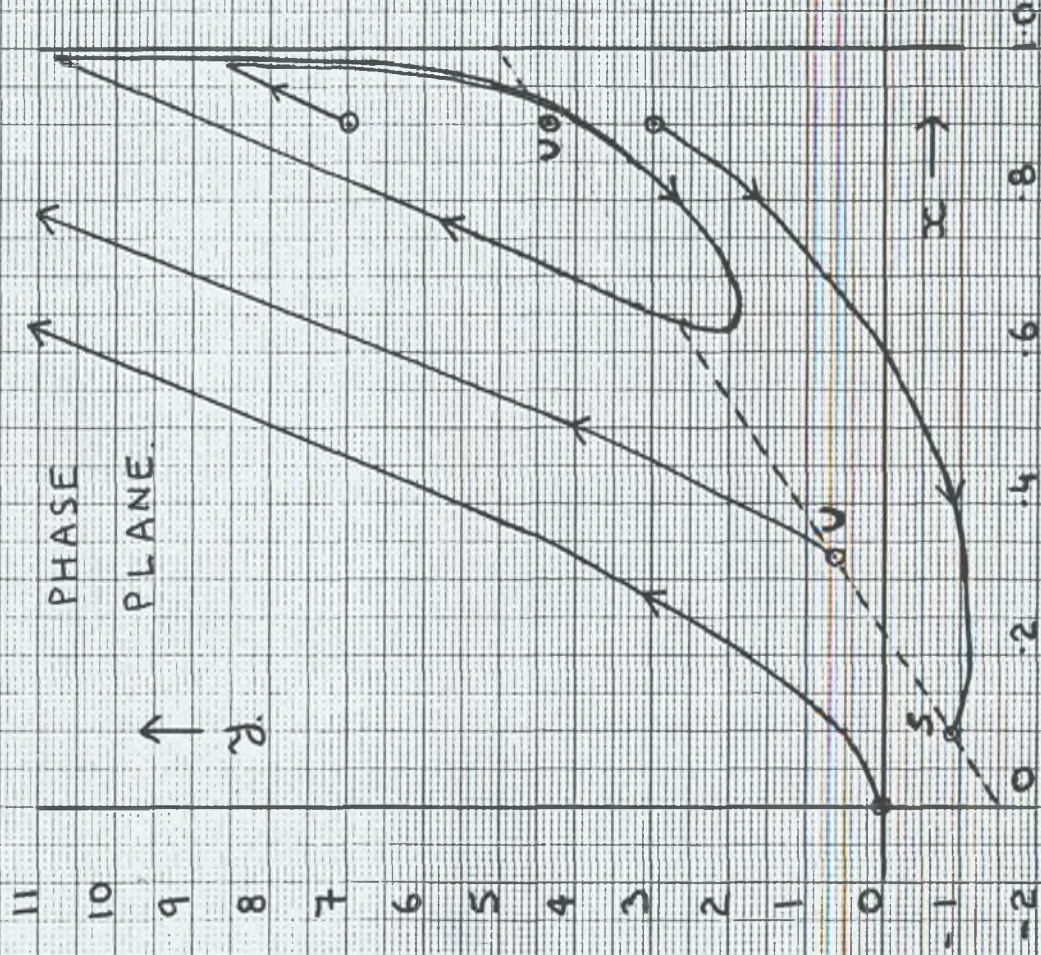
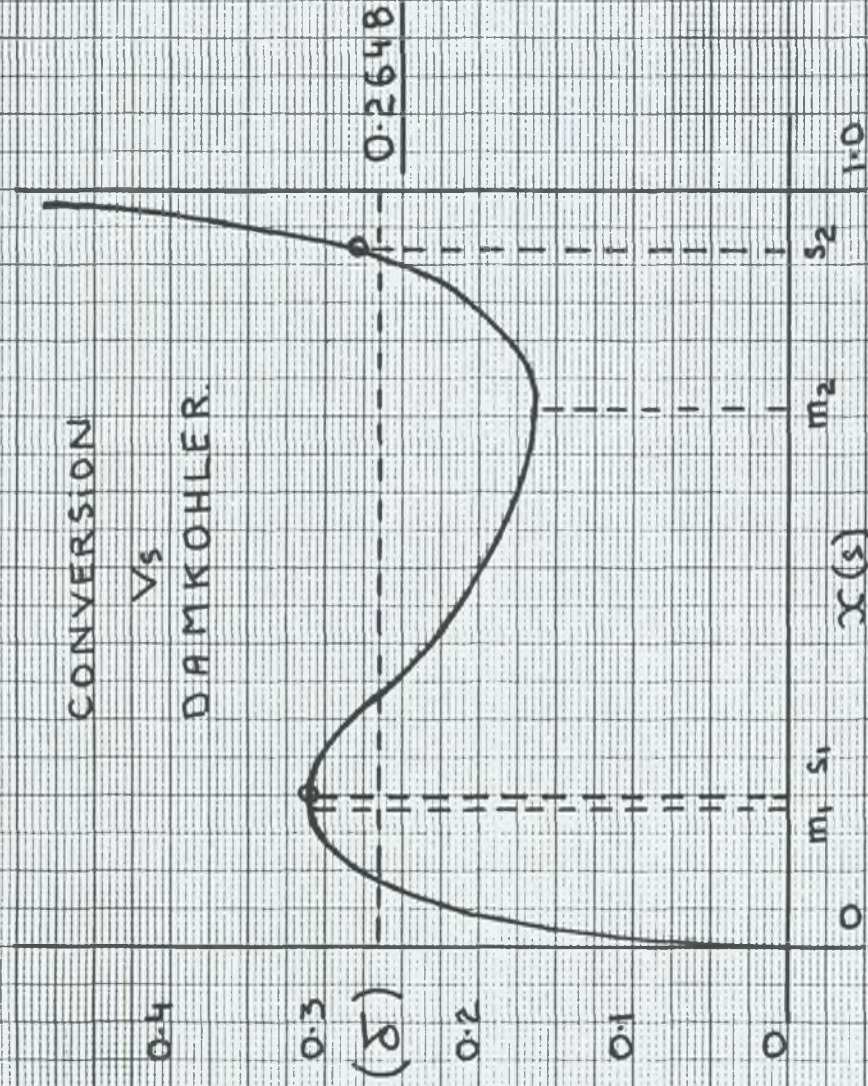


# REGION III.





# REGION IV.





The purpose of this section is to give a brief explanation of the nature of the graphs for the four qualitative regions taken as examples, and to relate these results to the C S.T.R. itself.

[A] Region I

For any given value of the Damkohler number only one steady state solution exists. This critical point, or equilibrium is globally asymptotically stable, as is depicted graphically by the phase portraits. The product conversion would give a 50% yield.

[B] Region II

Still only one critical point may exist, however it may now be either stable or unstable depending on the sign of the trace function which produces real roots at  $S_1$  and  $S_2$ .

In this example ( $\delta$ ) is chosen so that the equilibrium is stable but lies close to and below  $S_1$ .

Thus the critical point is surrounded by an unstable periodic orbit, which in turn is surrounded by a stable periodic orbit.

The phase portrait is quite complex about the equilibrium. All initial conditions starting outside the unstable periodic orbit will have phase trajectories converging to a stable periodic orbit (marked in red)

All initial conditions starting inside the unstable periodic orbit will tend towards the steady critical point, which again yields a 50% conversion

It should be noted that for the majority of initial conditions this system would tend to drive itself into a periodic equilibrium solution, yielding an interesting 'oscillating' situation for the process engineer.

-[C]      Region III      -

- Multiplicity of steady states now may occur as ( $\alpha$ ) has become large enough.

In this particular example all three of the steady states are unstable, due to appropriate selection of the Damkohler constant, and indeed these equilibria are surrounded by a very large stable periodic orbit.

Experimentally this would be a very interesting phenomenon to observe, with significant and rapid cyclic temperature and conversion variations occurring.

A further smaller decrease of the Damkohler constant would yield the graph of type shown in region IV. This would have manifested itself by a large reduction in the size of the periodic orbit and the evolution of one stable critical point.

[D]      Region IV

The evolution of a stable periodic orbit surrounding an unstable equilibrium as a parameter ( $\delta$ ) is perturbed is recognised as Hopfs Bifurcation. The bifurcation is strictly exhibited in this Region IV.

This phase plane is also characterised by the existence of a separatrix.

Clearly some initial conditions will tend to result in periodic orbit solutions whilst others will tend to the lower stable spiral equilibrium.

Exact determination of the separatrix would be possible by carefully 'reversing time' in the evolution equations and starting with an initial condition on one of the eigenvectors associated with the saddle point, which is always the middle of the three equilibrium points.

As one transgresses from region I to IV the Damkohler constant ( $\delta$ ) is decreased accordingly from 1.70 to 0.996 to 0.43106 to 0.2648 whilst the dimensionless group number ( $\alpha$ ) is increased from 8 to 12 to 20 to 26. This inverse relationship leaves potential for further studies.

Clearly, there is great scope for intriguing numerical work which is best supported by a clear understanding of the analytical work preceeding it.

These results only fringe on the scope for further studies. However, results are explicitly obtained and 'THEORY' (analytical work) and 'PRACTICE' (numerical work) do agree.

More significantly Hopf's Bifurcation phenomenon is described and evident in detail.

## CONCLUSIONS AND RECOMMENDATIONS

Oscillatory dynamical behaviour for a first order irreversible exothermic reaction in a continuous well stirred tank reactor without feedback control has been studied here in detail.

Material and enthalpy balances give rise to a two dimensional autonomous system of non-linear differential equations, which for certain parametric relationships may exhibit a multiplicity of steady states.

The author has concentrated on the evolution of bifurcating stable periodic orbits known as limit cycles through the application of Hopf's theorem for vector fields in  $R^2$ . Indeed, a direct link is established between the direction of bifurcation and the stability of the bifurcating orbit. Development of a stable closed orbit, known as supercritical bifurcation, is strictly referred to as Hopf Bifurcation.

The author pioneered the derivation of a detailed analytical expression the sign of which determines the stability of bifurcating periodic orbits for finite Arrhenius constant ( $\gamma$ )

This expression differs greatly from results of all other papers in that for finite  $\gamma$  the sign of the appropriate number  $\Delta'(0)$  depends only on the system parameters and not as in this case on the associated value of the critical points. Indeed, as is done in this text the value of the critical points may only be determined through numerical iterative procedures. The programme written covers dynamic behaviour in parametric space for finite ( $\gamma$ ).

-- Bifurcation to periodic orbits may only occur at points where the trace of the Jacobian vanishes provided that the strict crossing hypothesis of Hopf applies

This paper analyses the local nature of this theory, establishes the direction and stability of bifurcating orbits and then numerically analyses the branches of these solutions as the Damkohler parameter is perturbed. The model with proportional feedback control may give rise to new and interesting phenomena that may not already exist in the original system.

It is clear to the author that there is significant scope for further work on the dynamic response behaviour of the continuous stirred tank reactor specifically for the finite Damkohler case. Grounds for further detailed mathematical research would be to assume that the reactor is indeed not well stirred and this model would then give rise to a system of partial differential equations. Also in the light of technical developments in the industrial field, this model should be studied in conjunction with the proportional feedback controller case to develop a comprehensive understanding of the phase portraits possible and assist the engineer in obtaining reactor control and maximising product yield.

## APPENDIX A

### MULTIPLICITY CONDITION

Given  $g(x_s) = \frac{x_s}{1-x_s} \exp\left(\frac{-(dx_s + \beta\gamma_c)}{1+\beta + \frac{1}{\delta}(dx_s + \beta\gamma_c)}\right)$  Damkohler number A.1  
from Chapter 3.

then  $\frac{dg}{dx_s} = \frac{Q(x_s) \exp\left(\frac{-(dx_s + \beta\gamma_c)}{1+\beta + \frac{1}{\delta}(dx_s + \beta\gamma_c)}\right)}{(1-x_s)^2 \left(1+\beta + \frac{1}{\delta}(dx_s + \beta\gamma_c)\right)^2}$  A.2

where  $Q(x_s) = \left(\frac{d^2}{\delta^2} + d(1+\beta)\right)x_s^2 + \left(2\left(1+\beta + \frac{\beta\gamma_c}{\delta}\right)\frac{d}{\delta} - d(1+\beta)\right)x_s + \left(1+\beta + \frac{\beta\gamma_c}{\delta}\right)^2$  A.3

This quadratic function  $Q(x_s)$  has two roots: at  $m_1$  and  $m_2$  and  $Q(x_s) \leq 0$  for  $m_1 \leq x_s \leq m_2$ . These roots correspond to maxima and minima of the Damkohler function  $\delta = g(x_s)$  as shown below in Fig. A.1

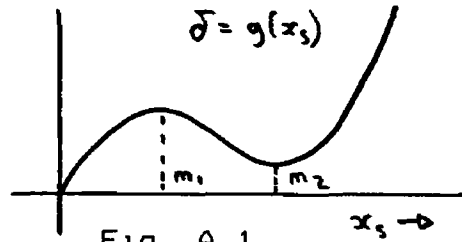


Fig. A 1

Thus  $m_1$  and  $m_2$  are the limit values of  $x_s$ , only within which multiplicity of steady state solutions may occur.

The solution set of  $\frac{dg}{dx_s} = Q(x_s) = 0$  yields the following

$$m_1, m_2 = \left\{ d \left[ \frac{2}{\delta} \left( 1 + \beta + \frac{\beta\gamma_c}{\delta} \right) - (1 + \beta) \right] \pm D_M^{1/2} \right\} / 2 \left( \frac{d^2}{\delta^2} + d(1 + \beta) \right) \quad A.4$$

where  $D_M = d \left\{ d \left[ \frac{2\beta\gamma_c}{\delta^2} + \left( \frac{2}{\delta} - 1 \right) (1 + \beta) \right]^2 - 4 \left[ 1 + \beta + \frac{\beta\gamma_c}{\delta} \right] \left[ \frac{d}{\delta^2} + (1 + \beta) \right] \right\}$  A.5

In order that  $m_1, m_2$  have real roots, then  $D_M \geq 0$  must be true which yields the desired result.

$$d \geq \left\{ \frac{4 \left( 1 + \beta + \frac{\beta\gamma_c}{\delta} \right)^2}{1 + \beta - \frac{4}{\delta} \left( 1 + \beta + \frac{\beta\gamma_c}{\delta} \right)} \right\} \quad \text{Q.E.D.} \quad A.6$$

## APPENDIX B

EVALUATION OF  $\text{DET } J_3$  AND  $\text{TR } J_3$  FUNCTIONS.

$$\text{Given } J_3 = \begin{pmatrix} \frac{-1}{1-x} & \frac{x}{(1+y/x)^2} \\ \frac{dx}{1-x} & -(1+\beta) + \frac{dx}{(1+y/x)^2} \end{pmatrix}_{\substack{x=x_3 \\ y=y_3}}$$

1)  $\text{DET } J_3$

$$\text{Det } J_3 = \left( \frac{1+\beta}{1-x_3} \right) + \left( \frac{dx_3^2 - dx_3}{(1-x_3)(1+y_3/x)^2} \right) \quad \text{from the Jacobian} \quad \text{B.1}$$

$$= \left( \frac{1+\beta}{1-x_3} \right) - \frac{dx_3}{(1+y_3/x)^2}$$

$$= \frac{(1+\beta)(1+y_3/x)^2 - (dx_3)(1-x_3)}{(1-x_3)(1+y_3/x)^2}$$

$$= \frac{1}{(1-x_3)(1+\beta)(1+y_3/x)^2} \left[ (dx_3^2 - dx_3)(1+\beta) + (1+\beta)^2(1+y_3/x)^2 \right]$$

$$= \frac{1}{(1-x_3)(1+\beta)(1+y_3/x)^2} [Q(x_3)] \quad \text{B.2}$$

$$\text{for } Q(x_3) = \left( \frac{d^2}{x^2} + d(1+\beta) \right) x_3^2 + \left( 2(1+\beta + \frac{\beta y_c}{x}) - d(1+\beta) \right) x_3 + \left( 1+\beta + \frac{\beta y_c}{x} \right)^2 \quad \text{B.3}$$

Thus the conditions  $\text{Det } J_3 = 0$  and  $\frac{dy}{dx} = 0$  } are synonymous.

and  $\text{Det } J_3 < 0$  defines steady states which are unstable saddle points. indeed this "slope condition" is a prerequisite for multiplicity of steady state solution sets.



## 2) TR $J_5$

By inspection of the Jacobian matrix

$$\begin{aligned} \text{Tr } J_5 &= \left( \frac{-1}{1-x} - (1+\beta) + \frac{dx}{(1+y/\delta)^2} \right) \quad \begin{matrix} x=x_1 \\ y=y_1 \end{matrix} \quad \text{B.4} \\ &= \frac{1}{(1-x)(1+y/\delta)^2} \left[ -\left( \frac{\delta(1+\beta)+dx+\beta\gamma_c}{\delta(1+\beta)} \right)^2 - (1+\beta)(1-x) \left( \frac{\delta(1+\beta)+dx+\beta\gamma_c}{\delta(1+\beta)} \right)^2 + dx(1-x) \right] \\ &= \frac{1}{(1-x)(1+y/\delta)^2} \cdot f(x) \end{aligned}$$

$$\begin{aligned} (\delta(1+\beta)+dx+\beta\gamma_c)^2 &= (d^2x^2 + 2d(\delta(1+\beta)+\beta\gamma_c)x + 2\beta\gamma_c\delta(1+\beta) + \delta^2(1+\beta)^2 + \beta^2\gamma_c^2) \\ f(x) &= \left\{ \frac{-(2+\beta)+x(1+\beta)}{\delta^2(1+\beta)^2} \cdot \left( d^2x^2 + 2d(\delta(1+\beta)+\beta\gamma_c)x + 2\beta\gamma_c\delta(1+\beta) + \delta^2(1+\beta)^2 + \beta^2\gamma_c^2 + dx - dx^2 \right) \right\} \quad \text{B.5} \\ &= +x^3 \left( \frac{d^2}{\delta^2(1+\beta)} \right) \\ &\quad - x^2 \left( d + \frac{(2+\beta)d^2}{\delta^2(1+\beta)^2} - \frac{2d}{\delta} - \frac{2d\beta\gamma_c}{\delta^2(1+\beta)} \right) \\ &\quad + x \left( d + (1+\beta) - \frac{2(2+\beta)d}{\delta(1+\beta)} - \frac{2\beta\gamma_c d(2+\beta)}{\delta^2(1+\beta)^2} + \frac{2\beta\gamma_c}{\delta} + \frac{\beta^2\gamma_c^2}{\delta^2(1+\beta)} \right) \\ &\quad - \left( 2+\beta + \frac{2(2+\beta)\beta\gamma_c}{\delta(1+\beta)} + (2+\beta) \left( \frac{\beta\gamma_c}{\delta(1+\beta)} \right)^2 \right) \end{aligned}$$

$$\text{For } \text{Tr } J_5 = \frac{d^2}{\delta^2(1+\beta)(1-x)(1+y/\delta)^2} \cdot (F(x)) \quad \text{B.6}$$

$$\text{Then } F(x) = x_1^3 + a_2 x_1^2 + a_1 x_1 + a_0 \quad \text{a cubic in } x_1 \quad \text{B.7}$$

where the constants  $a_2$ ,  $a_1$ , and  $a_0$  have been calculated as functions of  $d$ ,  $\beta$ ,  $\delta$ ,  $\gamma_c$  as given below.

$$\begin{aligned} a_2 &= - \left( \frac{\delta^2(1+\beta)}{d} + \frac{2+\beta}{1+\beta} - \frac{2(1+\beta)\delta}{d} - \frac{2\beta\gamma_c}{d} \right) \\ a_1 &= + \left( \frac{\delta^2(1+\beta)}{d} + \frac{\delta^2(1+\beta)^2}{d^2} - \frac{2(2+\beta)\delta}{d} - \frac{2\beta\gamma_c(2+\beta)}{d(1+\beta)} + \frac{2\beta\gamma_c\delta(1+\beta)}{d^2} + \left( \frac{\beta\gamma_c}{d} \right)^2 \right) \\ a_0 &= - \left( \frac{(2+\beta)(1+\beta)\delta^2}{d^2} + \frac{2(2+\beta)\beta\gamma_c\delta}{d^2} + \left( \frac{2+\beta}{1+\beta} \right) \left( \frac{\beta\gamma_c}{d} \right)^2 \right) \end{aligned}$$

## APPENDIX C

### ROOTS OF THE TRACE FUNCTION

Finding the roots of the trace function,  $\text{Tr } J(x_s) = 0$ , is equivalent to examining for the roots of the following cubic expression.

$$F(x) = x^3 + a_2 x^2 + a_1 x + a_0 \quad \text{C.1}$$

where  $a_2, a_1, a_0$  are given in Appendix B.

$$\text{and } F(0) = -\left(\frac{2+\beta}{1+\beta}\right)\left(\frac{\gamma(1+\beta) + \beta\gamma_c}{d}\right) < 0 \quad \text{C.2}$$

$$\text{and } F(1) = -\left(\frac{1}{1+\beta}\right)\left(\frac{\gamma(1+\beta) + d + \beta\gamma_c}{d}\right)^2 < 0 \quad \text{C.3}$$

Given the three roots of this expression as  $d_0, \beta_0, \gamma_0$ , that is

$$F(x) = x^3 - x^2(d_0 + \beta_0 + \gamma_0) + x(d_0\beta_0 + \beta_0\gamma_0 + \gamma_0d_0) - d_0\beta_0\gamma_0 \quad \text{C.4}$$

A typical plot of the trace function is as follows in Fig C.1

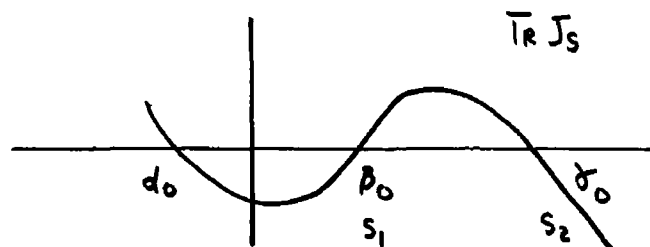


Fig C.1

The nature of this curve can be deduced from the sign of the constants  $a_2, a_1$ , and  $a_0$ , and the expression given for  $\text{Tr } J(x_s)$  in Appendix B.

This function will have two roots  $s_1$  and  $s_2$  where for some critical  $d$  it occurs that  $0 < s_1 = s_2 < 1$ . This condition will define the onset of instability.

## APPENDIX D

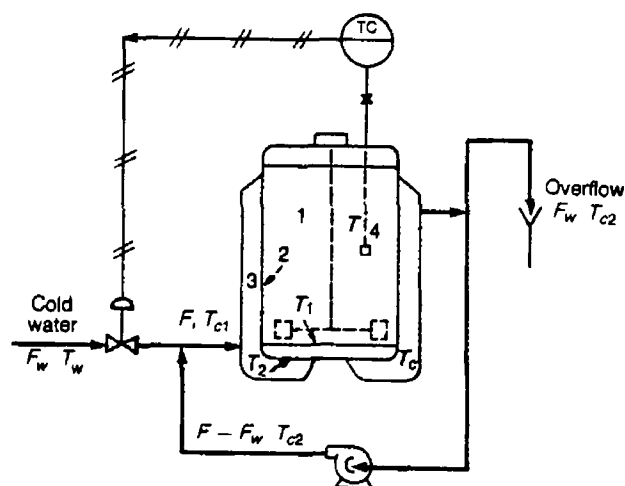
### CHEMICAL REACTOR - CONTROL THEORY

The potential benefits of advanced controls for continuous and batch reactors include increased productivity and improvements in safety, product quality, and batch to batch uniformity. Control loops will program temperature and pressure and maintain concentration and safety, while providing sequencing and record keeping functions.

In the case of an exothermic reaction the amount of heat generated increases as the reaction temperature rises. The addition of a feedback controller stabilizes an open loop unstable process only if the control loop is fast and does not contain too much 'deadtime'.

A real reactor has several lags and delays. The four interacting time-lags in a chemical reactor are shown below in Fig. D.1

Fig. D.1 7)



Time constants for the system are defined as follows, with typical values given:

Thermal:  $\tau_1 = (w_1 c_1 / \alpha) (T - T_1)$

Reactor Wall:  $\tau_2 = (w_2 c_2 / \alpha) (T - T_2)$

Coolant:  $\tau_3 = (w_3 c / \alpha) (T_2 - T_c)$

Thermal-bulb:  $\tau_4 = w_4 c_4 / R_1 A_4$

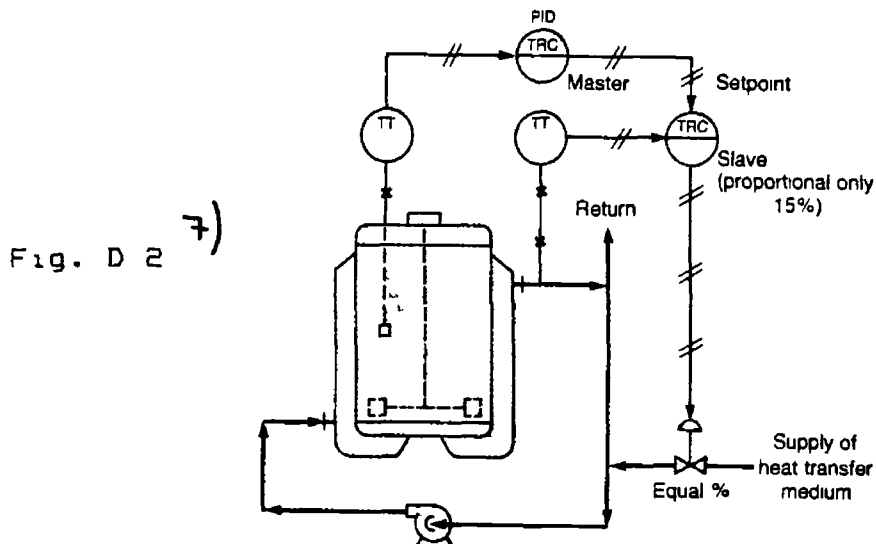
D.1

$W$  refers to the weight of element and  $C$  is its specific heat capacity.

In a well designed reactor, deadtime, should be held to less than 10% of the thermal time constant .

For good temperature control a recirculating cooling water system, where part of the coolant leaving the reactor jacket or cooling coils is pumped back to the coolant inlet, is desirable because it guarantees a constant high rate of water circulation This keeps the jacket deadtime constant, the heat transfer coefficient high, and eliminates cold and hot spots.

However cascade control, where two temperature controllers operate in series with the output of the reaction - temperature controller becoming the set point of the slave jacket - water temperature controller is very common. It is preferred that the slave controller maintain the jacket outlet and not the inlet temperature, because this way the jacket and its dynamic response is included in the slave loop. The period of oscillation of the master loop is usually cut in half as direct control is replaced by cascade as shown below in Figure D.2



In exothermic reactions one of the critical safety constraints is coolant availability. The reaction rate in a continuous reactor may be matched to the capacity of the cooling system. The optimizing controller detects the opening of the coolant valve and if it is less than 90% admits more feed by increasing the

set point of the flow recorder controller. When the coolant valve opens beyond 90% the production rate is lowered so that the reactor will never be allowed to run out of coolant. An ideal reactor temperature controller will permit rapid automatic rise to reaction temperature, without overshoot and will then accordingly control.

For highly unstable, accident prone reactors an added protective device can be provided, whose action is based on the permissible rate of temperature rise during heat up. This will prevent the process from building up thermal inertia as the region of potential instability is approached

A reactor control system should:

1. Provide the ability to maximise production
2. Minimise shutdowns
3. Maximise the percentage of ontime.
4. Minimise the variations in utility and raw-material demand.
5. Provide smooth operation in terms of constant conversion, yield and product distribution
6. Permit easy startup and shutdown.

However, the overriding, primary design objective is that the reactor must be safe for both the operating personnel and the environment

#### UNIT CONTROLLERS

A "Unit Controller" can control a plant unit operation - in a reactor, a distillation tower, a compressor, or any other subsystem. This represents a major step forward, because we will gradually stop thinking in terms of controlling single loops as pressures, flows or temperatures and will start thinking instead in multivariable terms - controlling the overall unit operation. High-level unit controllers also provide subroutines for scaling, automatic loop tuning, validity checks, and all those other features, that today involve substantial development risk and expense.

## IMPERFECT CONTROL

A servo-mechanism so perfect that signals of temperature deviation produce proportional changes in the flow rate of the coolant without either delay or error does not exist. In practice thermocouple readings will actuate a motor which will turn a valve and at all stages there will be errors and delays. Following the accepted practice of servo-mechanism theory, all these factors may be lumped into one transfer function.

It is important, though to find out whether the time lag of an imperfect system which is ultimately a proportional controller can destroy the possibility of control. However, to relieve the burden of analytical complexities, it will be assumed that a control system receives signals of the deviation of reactor temperature and uses them to give perfect proportional control of the rate of cooling,

Therefore chemical reactor with control from hence refers to a stirred tank reactor with "perfect proportional" control only

Stability "in the large" is determined by making extensive calculations on the full non linear equations describing the system thus obtaining phase plane portraits of the trajectories. Stability "in the small" may be determined by the first theorem of Lyapunov. The former requires considerable effort, and the latter gives no information on the size of the perturbation which is allowed. The second method or direct method of Lyapunov is a procedure which if successful would enable one to compute the size of the perturbation by defining a region of the phase plane inside of which, for a stable system, all temperatures would 'lead to a critical point'. The synthesis of these Lyapunov functions is more of an art than a science, as methods for the construction of a Lyapunov function for which the corresponding region of asymptotic stability is of significant size are not known for most non linear systems.

## A CONTROL MODEL - FOR THE C.S.T.R

Control of the reactor is accomplished by making the flow of the coolant through the reactor cooling coils a function of the reactor temperature.

The further the temperature of reactant A lies above the steady state temperature then the more the coolant flow control valve is open to enhance cooling and a more expedient approach to equilibrium

Formerly, heat was removed to the coolant at a rate  $Q$ , where:

$$Q = h A (T - T_c) \quad \text{J/sec} \quad \text{D.2}$$

$A$  ..... Coil surface area  $\text{m}^2$

$T_c$  .... Coolant temperature ( K )

$h$  ..... Heat transfer coefficient ( $\text{J/m}^2 \text{ K/sec}$ )

The heat transfer coefficient evaluated at steady state ( $h_s$ ), relates to the material of construction of the reactor and thermal properties of the constituents and is assumed constant over the temperature intervals concerned

$$\text{Thus} \quad Q = h_s A (T - T_c) \quad \text{D.3}$$

In the case of proportional control more heat is removed to the coolant by increasing the coolant flowrate. The degree of increase of coolant flowrate is directly proportional to the magnitude of the constituents temperature above steady state. <sup>10)</sup>

$$\text{Thus} \quad Q_p = h_s A (1 + K'(T - T_s))(T - T_c) \quad \text{D.4}$$

This simple linear interpolation will effect proportional control, and is the appropriate model for heat removal.

14)

The enthalpy balance with control now becomes

$$\rho V C_p \frac{dT}{dt} = \lambda \rho F C_p (T_F - T_0) + (-\Delta H) V R C - V U^* \quad D.5$$

where  $U^*$  is the heat removal rate to the coolant per unit volume. It is a function of  $T$  and the temperature and flow rate of the coolant.

Reparameterizing as before, and noting that

$$\gamma = \left( \frac{T - T_0}{T_0} \right) \cdot \delta \quad D.6$$

$$\text{and } K_p = \left( \frac{K' T_F}{\delta} \right) \quad D.7$$

$$f_1(x, y) = \dot{x} = -x + \delta(1-x) \exp\left(\frac{\gamma}{1+\gamma/\delta}\right) \quad D.8$$

$$f_2(x, y) = \dot{y} = -\gamma + \alpha \delta(1-x) \exp\left(\frac{\gamma}{1+\gamma/\delta}\right) - \beta(1+K_p(\gamma-\gamma_s))(\gamma-\gamma_c) \quad D.9$$

Some points worth noting;

- 1) The cooling term has now become a quadratic function in  $y$
- 2) At  $y = y_{s,j}$ :  $j = 1, 2, 3$ , whether there are one, two or three real solutions, then this two dimensional non linear system has the same steady state solution sets as the model without control.
- 3) The proportional control model is a localised one as  $y_{s,j}$  is specific to the steady state in question.

The Jacobian for this system at a particular steady state is

$$J_s(\bar{z}) = \begin{pmatrix} \frac{\partial f_1}{\partial x}, & \frac{\partial f_1}{\partial y} \\ \frac{\partial f_2}{\partial x}, & \frac{\partial f_2}{\partial y} \end{pmatrix}_{\substack{y=y_s \\ x=x_s}}$$

This new Jacobian now becomes

$$J_N = \begin{pmatrix} \frac{-1}{1-x_s}, & \frac{x_s}{(1+y_s/\delta)^2} \\ \frac{-\alpha x_s}{1-x_s}, & -(1+\beta) + \frac{\alpha x_s}{(1+y_s/\delta)^2} - \beta K_p(\gamma_s - \gamma_c) \end{pmatrix}$$



The Trace of the original system with cooling was

$$T_R(J_0) = \left( \frac{-1}{1-x_s} - (1+\beta) + \frac{dx_s}{(1+y_s/\delta)^2} \right). \quad D.10$$

The Determinant of the original system was

$$DET(J_0) = \left( \left( \frac{1+\beta}{1-x_s} \right) - \left( \frac{dx_s}{(1+y_s/\delta)^2} \right) \right) \quad D.11$$

For the model with control, these new functions now evolve as

$$T_R(J_N) = T_R(J_0) - \beta K_P (y_s - y_c) \quad D.12$$

$$DET(J_N) = DET(J_0) + \beta K_P \left( \frac{y_s - y_c}{1-x_s} \right) \quad D.13$$

Thus the stability of a critical point may be altered by proportional control.

In examining the nature of stability of the C.S.T.R. with control one must firstly examine the sign of the Trace and Determinant functions as given above.

The following two axioms are a basis for the control rationale.

$$1) \quad T_s > T_c$$

This means that cooling is occurring: not heating. That is, at steady state heat is being removed from the reactor. This is a thermodynamic prerequisite, as the reaction is exothermic, and the rate of heat generation will equal the rate of heat removal at steady state.

Dimensionlessly this implies that;

$$y_s - y_c > 0$$

$$2) \quad 0 < C_{a,s} < C_{a,F}$$

This means that at steady state, the concentration of species A in the reactor is always less than the feed concentration. This is because A is being converted to B

$$\Rightarrow \quad 0 < \frac{C_{a,s}}{C_{a,F}} < 1$$

Dimensionlessly, this implies that;

$$0 < (1-x_s) < 1$$

From the above two expressions it follows that

$$(\gamma_s - \gamma_c) > 0 \quad \text{D.14}$$

$$\left( \frac{\gamma_s - \gamma_c}{1 - x_s} \right) > 0 \quad \text{D.15}$$

$$\text{Given } \phi = \phi(\beta, \gamma_s, \gamma_c) = \beta(\gamma_s - \gamma_c). \quad \text{D.16}$$

$$\text{and } \Theta = \Theta(\beta, \gamma_s, x_s, \gamma_c) = \beta \left( \frac{\gamma_s - \gamma_c}{1 - x_s} \right) \quad \text{D.17}$$

where  $\phi$  and  $\Theta$  are strictly positive functions in the domain specified for this problem then the control model may be further abbreviated as follows.

$$T_R(J_N) = T_R(J_0) - K_P \phi \quad \text{D.18}$$

$$D E T(J_N) = D E T(J_0) + K_P \Theta \quad \text{D.19}$$

It directly follows that  $T_R(J_N)$  may always be made negative, and  $D E T(J_N)$  may always be made positive by choice of a suitably positive value of  $K_P$ ; where  $K_P$  is the perfect variable proportional feedback controller gain.

Proof of the following proposition now becomes immediate by employing the ROUTH - HURWITZ criteria.

Proposition D.1 Given that the response of a perfect controller is proportional to the deviation from "steady state" then local asymptotic control may always be attained by sufficient amplification of the signal.

Corollary D.2 If  $(x_s, u_s)$  is stable without control, then for  $K_p \geq 0$ , it remains stable with control.

Proof D.2

$$\text{Given } \text{Tr}(J_0) < 0$$

$$\text{and } \text{DET}(J_0) > 0$$

$$\text{then for } \text{Tr}(J_N) = \text{Tr}(J_0) - K_p \phi$$

$$\text{and } \text{DET}(J_N) = \text{DET}(J_0) + K_p \theta$$

where  $\phi, \theta, K_p$  are all positive

$$\text{then } \text{Tr}(J_N) < 0$$

$$\text{and } \text{DET}(J_N) > 0$$

and stability with control is still attained.

Corollary D 3 For  $K_p \geq 0$ , local control improves stability of the steady state solution set

Proof D 3

From D.2 it follows

$$\text{Tr}(J_N) < \text{Tr}(J_0)$$

$$\text{and } \text{DET}(J_N) > \text{DET}(J_0)$$

$$\text{Noting } \lambda_N^2 - (\text{Tr}(J_N))\lambda_N + \text{DET}(J_N) = 0$$

$$\text{then } \lambda_N = (\text{Tr}(J_N) \pm \sqrt{\Delta_N}) / 2$$

$$\text{where } \Delta_N = (\text{Tr}(J_N))^2 - 4 \text{DET}(J_N).$$

then the eigenvalues of the Jacobian become more negative and stability is strengthened.

$$\text{IE } \lambda_N < \lambda_0 < 0.$$

D.20

The rate of approach to equilibrium is accelerated.

## NUMERICAL EXAMPLE OF PROPORTIONAL CONTROL - SADDLE POINT

Assumption: Coolant and feed temperatures are equal throughout the reaction.

Given:  $\alpha = 22$ ,  $\beta = 3$ ,  $\gamma_c = 0$ ,  $\delta = 20$ ,  $\bar{\delta} = 0.9$ ,

Comment: Multiplicity exists, by section 3.2.

One solution set is

|                        |                   |
|------------------------|-------------------|
| $x_s = 0.46559$        | A saddle point    |
| $\gamma_s = 2.56072$   |                   |
| $TR(J_0) = 2.1784 > 0$ | From programme    |
| $DET(J_0) = -5648 < 0$ | numerical results |

Examining the control model yields the following calculations

$$\begin{aligned}
 \gamma_s - \gamma_c &= 2.56072 \\
 1 - x_s &= 0.53441 \\
 \phi_s &= 7.68216 \\
 \Theta_s &= 14.37503
 \end{aligned}$$

and

$$\begin{aligned}
 TR(J_N) &= 2.1784 - K_p 7.68216 \\
 DET(J_N) &= -5648 + K_p 14.37503 \\
 TR(J_N) &= 0 \quad \text{if } K_p = 0.2836 \\
 DET(J_N) &= 0 \quad \text{if } K_p = 0.0393
 \end{aligned}$$

Conclusion: Local stability requires  $K_p > 0.284$

Thus for  $K_p \geq 1$ , a rapid approach to a stable steady state, which originally was unstable without control, will be achieved. 4)

## BIBLIOGRAPHY

- 1) Braun, M  
"Differential Equations and Their Applications"  
Springer - Verlag , (1983).
- 2) Crandall, M G. and Rabinowitz, P.H  
"Mathematical Theory of Bifurcation" in,  
Bifurcation Phenomena in Math Physics  
C Bardos and D Bessis editors  
Reidel., (1980)
- 3) Hirsh, M. and Smale, S  
"Differential Equations, Dynamical Systems and  
Linear Algebra".  
Academic - Press., (1974)
- 4) Hyun, C J. and Aris, R  
"The Control of a Stirred Tank Reactor with  
Hysteresis in the Control Element"  
Chem Eng. Sci., 27, 1341, (1971)
- 5) Iooss, G and Joseph, D D  
"Elementary Stability and Bifurcation Theory"  
Springer - Verlag , (1980)
- 6) Levenspiel, O.  
"Chemical Reaction Engineering"  
Wiley , 2nd ED ,326, (1972).
- 7) Liptak, B G  
"Controlling and Optimising Chemical Reactors"  
Chemical Engineering, May 26, 69 ,(1986).

- 8) Marsden, J and McCracken, M.  
"The Hopf Bifurcation and its Applications"  
Springer - Verlag , (1976)
- 9) Perry, R.H and Chilton, C H.  
"Chemical Engineers Handbook"  
McGraw - Hill , 5th ED
- 10) Perlmutter, D.D  
"Stability of Chemical Reactors"  
Prentice - Hall , (1972)
- 11) Poore, A B  
"A Model Equation arising from Chemical Reactor  
Theory"  
Archive for Rational Mechanics and Analysis , 52,  
358, (1973).
- 12) Sanchez, D  
"Ordinary Differential Equations and Stability  
Theory"  
Freeman , (1968).
- 13) Uppal, A , Ray, W H , and Poore, A B  
"On the Dynamic Behaviour of Continuous Stirred  
Tank Reactors"  
Chem Eng Sci , 29, 976, (1974)
- 14) Warden, R.B , Aris, R , and Amundson, N R  
"An Analysis of Chemical Reactor Stability and  
Control"  
Chem Eng Sci., 19, 149, (1964)