

Frontiers in Chemical Reaction Engineering

VOLUME I

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Frontiers in Chemical Reaction
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Volume 1

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PREFACE

The foundations of modern chemical reaction engineering can be traced to the publication 1947 of Part III, **Kinetics and Catalysis of Chemical Process Principles** by Professors O.A. Hougen and K.M. Watson. True, modern mathematical methods of analysis were absent in this book, and a solitary procedure of designing a fixed-bed reactor was all that it contained by way of design and analysis as we understand it today. This book, however, inspired many other attempts in the general area of chemical reactor design which was subsequently (perhaps about ten years later) christened, by nobody in particular, as chemical reaction engineering and popularised through the book **Chemical Reaction Engineering** by Professor Octave Levenspiel. Chemical reactions are ubiquitous, and cannot be restrained by any boundaries. What started out principally as analysis and design of catalytic and gas-liquid reactors today encompasses a variety of reacting systems such as polymeric, biochemical, electrochemical, nuclear, environmental, etc.

There is considerable interest among the international community of chemical engineers to periodically meet and exchange views and results of research in this constantly widening field. As a natural consequence of this interest, the European Federation of Chemical Engineering has undertaken to organize at intervals of two years International Symposia on Chemical Reaction Engineering (ISCRE). Seven such symposia have so far been organized, alternately in Europe and USA, and the eighth symposium is scheduled to be held in Edinburgh later in 1984. The Poona symposium **International Chemical Reaction Engineering Conference (ICREC)** may be regarded as a complementary effort, with the primary objective of assembling at the National Chemical Laboratory renowned researchers in chemical reaction engineering and organizing plenary lectures as well as lectures outlining the results of research in specific areas. Another objective of this conference is to focus attention of the world community of chemical engineers on the fact that chemical reaction engineering occupies a preeminent position not only in Europe and USA, but in many Asian and other countries as well, particularly in India. As will be seen from the list of plenary lectures and papers presented, there are authors from China, Japan, India and Australia.

Coincidental but important is the remarkable fact that a number of events pertaining to chemical engineering have been taking place at the National Chemical Laboratory during the last year or two. A book titled **Three-Phase Catalytic Reactors** by P.A. Ramachandran and R.V. Chaudhari (Gordon and Breach) was published a few months ago. The first three volumes of the series **Advances in Transport Processes** (Wiley Eastern) jointly edited by A. Mujumdar of McGill University and R.A. Mashelkar of National Chemical Laboratory have already appeared (there are in these issues several articles pertaining to chemical reaction engineering). A two-volume treatise titled **Heterogeneous Reactions: Analysis, Examples and Reactor Design** by M.M. Sharma of the University of Bombay and L.K. Doraiswamy of the National Chemical Laboratory (Wiley Interscience) is expected to be published in January 1984. Additionally, one of the editors of the present volume (L.K.D.) has also edited another book titled **Recent Advances in the Engineering Analysis of Chemically Reacting Systems**. This book, which is a **Special Number** of the Indian Chemical Engineer (the official journal of the Indian Institute of Chemical Engineers) is also expected to be published around the same time as the present volumes. These facts are being mentioned, not to specifically bring out the contributions of this laboratory in chemical reaction engineering, but rather to emphasize the fact that the organization of this conference at this laboratory has been a natural consequence of the spurt of activity in this country in general and in this laboratory in particular.

A total of 81 articles consisting of 14 plenary lectures and 67 research papers will be presented at the conference. Since these constitute approximately 1200 pages it was decided to publish them in two volumes. Thus the proceedings of this conference which covers gas-solid catalytic and noncatalytic reactors, multiphase reactors, fluid bed reactors, steady state and dynamic behavior, biochemical engineering, polymeric reacting systems, and general articles, will appear in two volumes organized as follows:

Volume I

- Plenary lectures
- Multiphase reactors
- Biochemical reactors
- Polymerization reactors
- General

Volume II

- Gas-solid catalytic and noncatalytic reactors
- Dynamics and stability
- Fluidized bed reactors

Although the coverage of chemical reaction engineering in these volumes is by no means complete, one cannot fail to see that many important aspects of the subject have been included. The plenary

lectures provide a fascinating mix of theory, experiment and practice. The research papers tend to continue this trend. A feature of the conference, which unfortunately cannot be covered in these volumes, is a panel discussion on **Frontiers in Chemical Reaction Engineering** with experts drawn from the academia and industry. This promises to be a very exciting discussion.

Editing such a heterogeneous mix of articles from different countries is indeed a mammoth task. One of the thrusts of our editorial policy was to retain the authenticity of the original articles to the fullest extent possible. As a result some nonuniformities in the papers may be noticed, such as: retention of American and English spellings, variations in the style of referencing both in the body of the text and under references, and in the placement of figures.

In organizing a symposium of this magnitude, considerable assistance is necessary not only from different agencies in terms of financial support but also from colleagues and coworkers in matters of correspondence, assembling of papers, making editorial corrections, organizing the material, and in a number of other ways which cannot be recorded. The financial support received by the organizers from a number of agencies is acknowledged separately in each of these volumes. We would also like to take this opportunity of expressing our deep sense of gratitude to those organizations without whose enthusiastic support this conference would not have been possible. In particular we would like to mention the Council of Scientific and Industrial Research (of which this laboratory is a constituent), Indian Oil Corporation, Indian Petrochemicals Corporation Ltd, Tata Chemicals Ltd, Hindustan Organic Chemicals Ltd, Alchemie Research Centre, Hico Products Ltd, and Hindustan Lever Ltd.

In the scientific organization of the programme we have received assistance from a number of our colleagues and students. In particular we would like to place on record our deep sense of gratitude to Dr. B.D. Kulkarni for the invaluable help rendered by him. He has helped both as joint secretary of this conference and as a chemical engineer gifted with an incisive mind and originality. We are also grateful to Dr. Ravi Kumar, Mr. S.S. Tambe, and Mr. N.S. Dabke. A major event such as ICREC cannot be successful without the enthusiastic support of a large number of persons. We wish to place on record our sincere appreciation of the untiring efforts of numerous individuals from NCL, who gave of their best. Indeed, the dedicated effort of the entire infrastructure of NCL has been responsible for this success. The cheerful support received from the secretarial staff and the draughtsmen is particularly appreciated. The assistance of Dr. S.H. Iqbal, Head of the Division of Technical Services of NCL, and Mr. M.M. Sharma, Administrative Officer of NCL, has been most invaluable. The organization of this symposium started out with a great deal of enthusiasm in 1981. The National Organising Committee has been of great help, in particular Professor M.M. Sharma to whom we have often turned for help and advice.

Among the galaxy of internationally renowned scientists who have contributed to this conference, one unique personality we have sadly missed is Professor Neal Amundson. He was to have presented a keynote lecture entitled 'Early Developments in Chemical Reaction Engineering', but had to withdraw due to ill-health. This was most unfortunate since modern chemical engineering owes much to Professor Amundson, and his views and reflections on the developments would have been of immense value.

The quality of a conference of this type is judged largely by the quality of the individual contributions. We wish to record our sincere thanks to the plenary lecturers and panelists who readily responded to our invitation: G. Allen, R. Aris, G. Astarita, K.B. Bischoff, G. Boreskov, J.B. Butt, J.B. Cropley, J.F. Davidson, G. Froment, V. Hlavacek, H. Hofmann, D. Luss, O.E. Potter, D. Ramkrishna, W.H. Ray, M.M. Sharma, Y.T. Shah, W.E. Stewart, A. Varma, J. Villadsen, V. Weekman and J. Wei. We wish to thank Dr. Haldar Topsoe for agreeing to give the inaugural address and Prof. M.G.K. Menon, Member, Planning Commission, and one of the foremost scientists of this country, for having agreed to give the valedictory address.

It is pleasant to record that the enthusiasm with which we launched this effort did not show any abatement as the months passed, and the response from the international community of chemical engineers was uniformly spontaneous and encouraging. At the time of writing this preface the conference has not yet taken place, and we hope we shall have the good fortune to say that all those who accepted our invitation have indeed attended and that the conference has been a uniquely successful one.

Carried away by the overwhelming response we received and our own waxing enthusiasm, we had visions during the last two years of making this conference a periodic event at this laboratory. The effort, expense and local persuasions involved are so heavy and taxing that we are not sure at this time whether we would not be content to leave this as a one-time effort. If we may end on a personal note, the encouragement and cooperation we have received and the friendships we have cultivated from chemical engineers through out the world have been the most rewarding and lasting experience of this fascinating endeavour.

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PLENARY LECTURES

Some Problems in the Dynamics of Chemical Reactors

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SUMMARY

1. Two important problems in the dynamics of chemical reactors are the description of the various steady states or limit cycles and the phenomenon of period doubling leading to chaos. These are discussed through the analysis of a stirred tank in which the consecutive reactions $A \rightarrow B \rightarrow C$ are taking place.

INTRODUCTION

2. In the 'real' world of chemical reactors the plant operator's dream is attained in the stable and efficient performance of his charge, fed by a steady input stream and untroubled by having to accommodate any downstream disasters. The enterprising will, of course, enjoy the transients of start-up and the adventurous may essay the hill of optimality by evolutionary operation or questing control, but the practical man will, by and large, be better pleased with static efficiency than with dynamic excitement. Though it has been known for some time that the mean output of an oscillating system may sometimes have the advantage over adjacent steady states, the temerity to put this into operation is rare. Of course it is known that some reactors are "difficult to control," that others get into a cyclic mode of themselves, that temperatures "run away" and that a change of input sometimes produces the opposite of the expected effect.

3. These phenomena are all reflected in the waters of theoretical chemical reaction engineering, a world of deep analyses where Neptune's court, long since perturbed into action by the shadow of the engineering Argonauts' ship, has been busy with its equations and their solutions. In this world of model systems all of the observed phenomena can be examined in detail and, if there can be discovered depths of fascinating behavior that have as yet no original in the imaged world, it must be remembered that there are heights of complexity and delicacy in aerae that have as yet counterpart in alta.

4. Professor Amundson has reviewed the way in which some of the key insights into chemical reaction engineering developed and it has been a rare privilege to have this from dux ipse (Refs. 1,2). I shall attempt neither a historical reflection nor a complete survey, but take refuge in the eclecticism of the title and consider only two of the many interesting problems in the dynamics of reactors. These have to do with global portraits and to the generation of chaos through repeated bifurcation of periodic solutions.

GLOBAL PORTRAITS

5. Only a few years ago it was possible to think in terms of a fairly simple picture of the reactor as a dynamical system (Ref. 3). It might have a finite number of invariant sets, some stable and others unstable. The first of these to be recognized were the steady states and their linearized portraits were seen to be good descriptions of local

behaviour. Limit cycles were first discovered in systems with control (Ref. 4) and appeared later with more complex systems (Ref. 5). To each stable invariant set belonged an open subset of state-space which was its region of attraction, while the unstable were embedded in closed subspaces within which they were attractors and which served as separatrices for the regions of attraction of the stable states. The number of invariant sets could often be proved odd, the stable being even in number and the unstable odd (Ref. 6).

6. That the picture of even the simplest system could be vastly more complicated was perhaps first clearly brought out in the work of Uppal, Ray and Poore (Refs. 7,8) who took up again the simplest case of a stirred tank reactor with a single exothermic reaction. They were able to survey the scope of parameter space and discern regions within which the phase portraits of the system (in this case phase-planes in concentration and temperature) were qualitatively the same. Now limit cycles within limit cycles and multiple steady states within these were seen to occur, yet even they did not discover the full complexity of the picture (cf. Refs. 9,10) and, who knows whether there may not be further details left to discover.

7. The sequential reaction scheme $A \rightarrow B \rightarrow C$ was early mentioned, Amundson and Bilous (Ref. 11) showing that there could be five steady states but was not much studied until Hlaváček and his colleagues took it up (Ref 12). They explored the multiplicities and stability transitions of this system, and it was left to Poore, Hable, Heineman, and Doedel (Refs 13, 14) to develop the dynamics.

8. Here it should be said that for each irreversible reaction in a stirred tank reactor there are three parameters: α , a Damkohler number; β , a dimensionless heat of reaction; and γ , an Arrhenius number or dimensionless heat of reaction. For each reversible reaction there will be five parameters while for the reactor itself there is at least one parameter related to the cooling rate. Thus for $A \rightarrow B \rightarrow C$ there are seven parameters, six of which are related to the kinetics and one being an operating variable. In a space of seven dimensions a chimaera or even a hippalectryon might lurk undisturbed and we shall mention later at least one strange structure (Ref. 15) that is to be found there. A popular move, but one whose ultimate justification has yet to be fully demonstrated is to let $\gamma \rightarrow \infty$ and this has the merit of removing one parameter.

9. The equations for a stirred tank with a feed of pure A and in which the reactions $A \rightarrow B \rightarrow C$ are taking place are three in number for u and v , the dimensionless concentrations of A and B, and w , the dimensionless temperature. The detail of their derivation is given in Ref. 15 and the nomenclature is fully explained at the end of this paper. They are:

$$\dot{u} = 1 - u\{1 + \alpha E(w)\}, \quad (1)$$

$$\dot{v} = \alpha u E(w) - v\{1 + \alpha \sigma E^v(w)\} \quad (2)$$

$$\dot{w} = -(1 + \kappa)w + \alpha \beta u E(w) + \alpha \beta \rho \sigma v E^v(w), \quad (3)$$

where $E(w) = \exp\{\gamma w / (\gamma + w)\}$, (4)

which reduces to $\exp w$ if $\gamma \rightarrow \infty$.

10. At a steady state (u_s, v_s, w_s)

$$u_s = \{1 + \alpha E(w_s)\}^{-1} \quad (5)$$

$$v_s = [\alpha E(w_s) / \{1 + \alpha E(w_s)\}] \{1 + \alpha \sigma E^v(w_s)\}^{-1} \quad (6)$$

and substituting these in Eq. 3 gives

$$\sigma E^{v+1}(w_s) \{\beta(1 + \rho) - (1 + \kappa)w_s\} \alpha^2 + E(w_s) \{\beta - (1 + \kappa)w_s [1 + \sigma E^{v-1}(w_s)]\} \alpha - (1 + \kappa)w_s = 0. \quad (7)$$

This equation is capable of having five roots for suitable combinations of $\alpha, \beta, \gamma, \kappa, v, \rho$ and σ , and it was the analysis of this situation that was initiated by Hlaváček and his colleagues (Ref. 12). They showed that it was better to treat w_s as a parameter and solve the quadratic (Eq. 7) for α , since there is only one positive root for α . The eigenvalues of the linearization at (u_s, v_s, w_s) can then be calculated and the local character of the steady state is fully known. For fixed $\beta, \gamma, \kappa, v, \rho, \sigma$ a curve of w_s versus α can be drawn as in Fig. 1 for which $\beta=9, \gamma=\infty, \kappa=v=\rho=1, \sigma=0.01$. Where the line is solid the steady state is stable, but it is unstable between J1 and 4 and between J3 and 7. The points J1, ...J4 are where a real eigenvalue goes through the origin but 4 and 7 are Hopf bifurcation points. Using the criteria for this type of bifurcation (See Ref. 16) it can be shown that near the points 4 and 7 on the segments 3-4 and 6-7 there is a stable limit cycle which contracts around the steady state as α approaches

α_4 or α_7 .

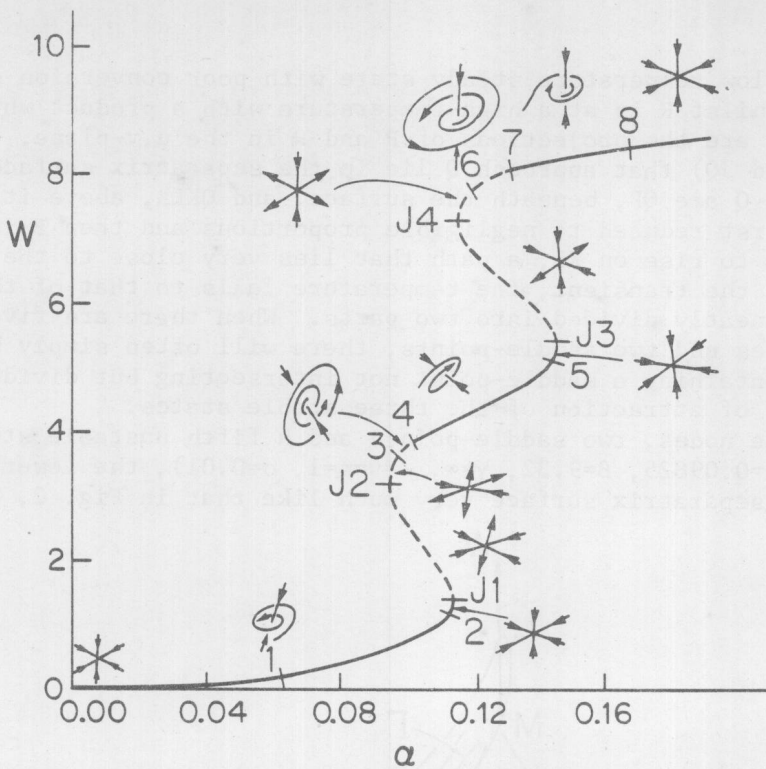


Figure 1 Steady-state temperature and stability as a function of Damkohler number

11. Extensive calculations have been done by D.V. Jorgensen (Ref. 17) both of α, w -curves, such as in Fig. 1 and of regions consistent dynamics in the α, β -plane. This is not the place for full exposition of her results, but it is appropriate to show some of the three dimensional phase portraits as they have important implications for the dynamics of the system. Consider first the relatively simple situation in which there are three steady states ($\alpha=0.083, \beta=10.8, \gamma=\infty, \kappa=\nu=\rho=1, \sigma=0.01$), shown as P, Q, and R in Fig. 2. Here P lies below the separatrix surface DEGH, Q in it and R above it, near

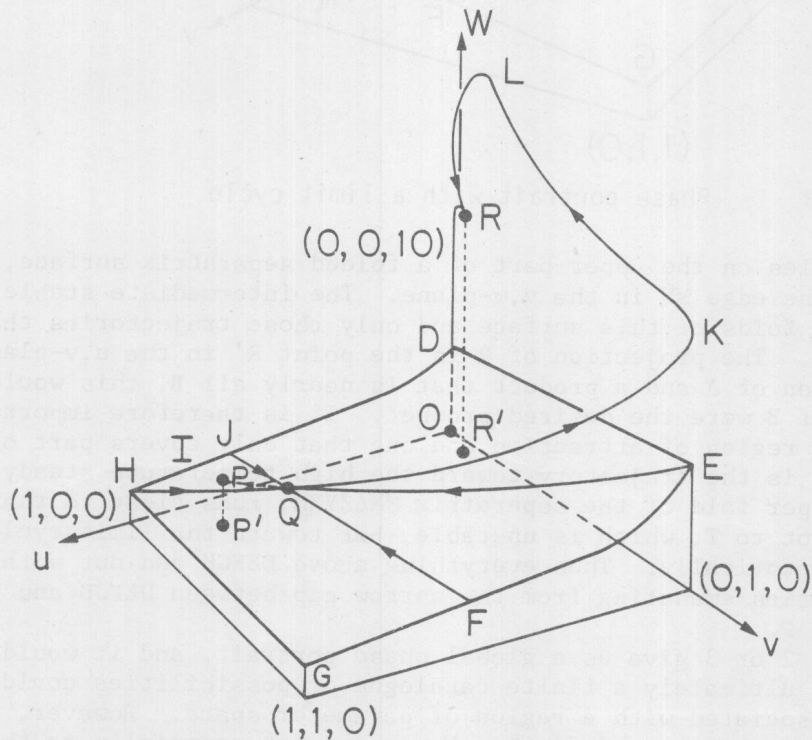


Figure 2 Phase portrait with multiple steady-states

the w -axis. Clearly P is a low temperature steady state with poor conversion of A to B and little formation of C , whilst R is at a high temperature with a product which is almost entirely C ; P' and R' are the projections of P and R in the u,v -plane. The four trajectories (EQ , FQ , IQ , and JQ) that approach Q lie in the separatrix surface $DEGH$. The two trajectories leaving Q are QP , beneath the surface, and $QKLR$, above it. On $QKLR$ the concentration of A is first reduced to negligible proportions and then B is consumed as the temperature continues to rise on KL , a path that lies very close to the v,w -plane; in the final stage of the transient, the temperature falls to that of the steady state. Thus state space is neatly divided into two parts. When there are five steady states with three stable nodes and two saddle-points, there will often simply be two separatrix surfaces, each containing a saddle-point not intersecting but dividing the space into the three regions of attraction of the three stable states.

12. When there are two stable nodes, two saddle-points and a fifth unstable steady state with a nearby limit cycle ($\alpha=0.09825$, $\beta=9.32$, $\gamma=\infty$, $\kappa=\nu=\rho=1$, $\sigma=0.01$), the lower saddle-point, Q in Fig. 3, is in a separatrix surface very much like that in Fig. 2, but the

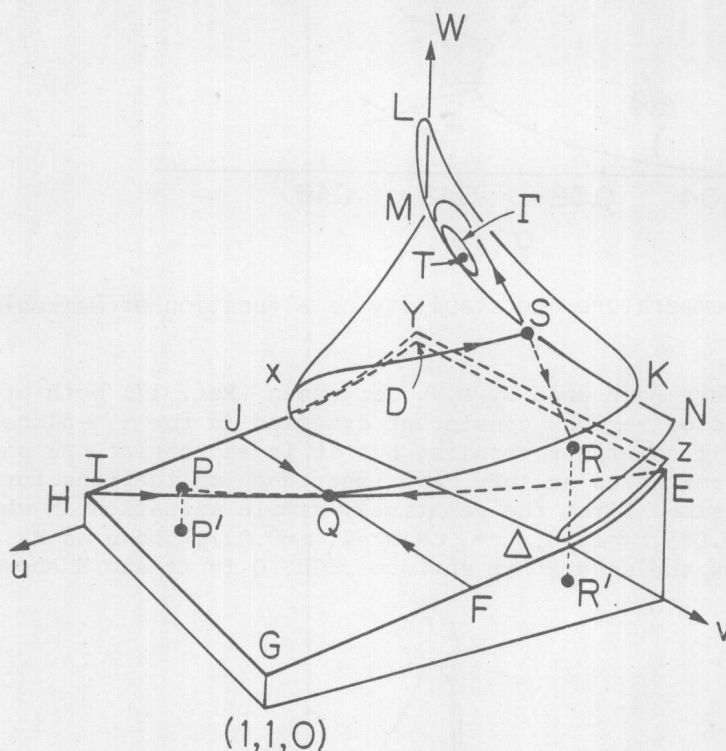


Figure 3 Phase portrait with a limit cycle

upper saddle-point, S , lies on the upper part of a folded separatrix surface, $MN\Delta ZYXM$, very close to the edge MN in the v,w -plane. The intermediate stable steady-state R lies between the folds of this surface and only those trajectories that start within this fold go to R . The projection of R is the point R' in the u,v -plane. Since this has a good conversion of A and a product that is nearly all B , this would be the desirable steady-state if B were the desired product. It is therefore important to know that it has a small region of attraction and one that only covers part of the u,v -plane. The path QKL is the trajectory toward the high temperature steady-state, T , which passes over the upper fold of the separatrix $MN\Delta ZYXM$, runs close to the v,w -plane from K to L , and drops not to T , which is unstable, but toward the limit cycle, Γ , which it approaches asymptotically. Thus everything above $DEFGH$ and not within the fold, including trajectories emanating from the narrow gap between $DEFJD$ and $YZ\Delta XY$, goes to the limit cycle, Γ .

13. Figures such as Fig. 2 or 3 give us a global phase portrait, and it would be attractive to think that ultimately a finite catalogue of possibilities could be assembled, each item being associated with a region of parameter space. However, the vastness of this seven dimensional space defies such an approach especially as the fineness of the division of parameter space is itself barely specifiable in certain one dimensional transections (Ref. 15). Moreover, the regions of attraction in the presence of chaos are themselves virtually as complex as a Cantor set and require a cultivated

imagination if they are to be apprehended to any degree. Let us turn to this aspect of the dynamics of reactors.

PERIOD DOUBLING

14. There are regions of the parameter space of the stirred tank with $A \rightarrow B \rightarrow C$ for which only a single, unstable steady-state exists. Since this has a region of attraction of measure zero, there must be some other structure which is stable. Such a region is $\alpha=0.55$, $\beta=17.5$, $\gamma=\infty$, $\nu=\rho=1$, $\sigma=0.01$, and $5.600 \leq \kappa \leq 6.949$. In this region there is a limit cycle of the form of PQR in Fig. 4. Like some of the trajectories we have seen it goes

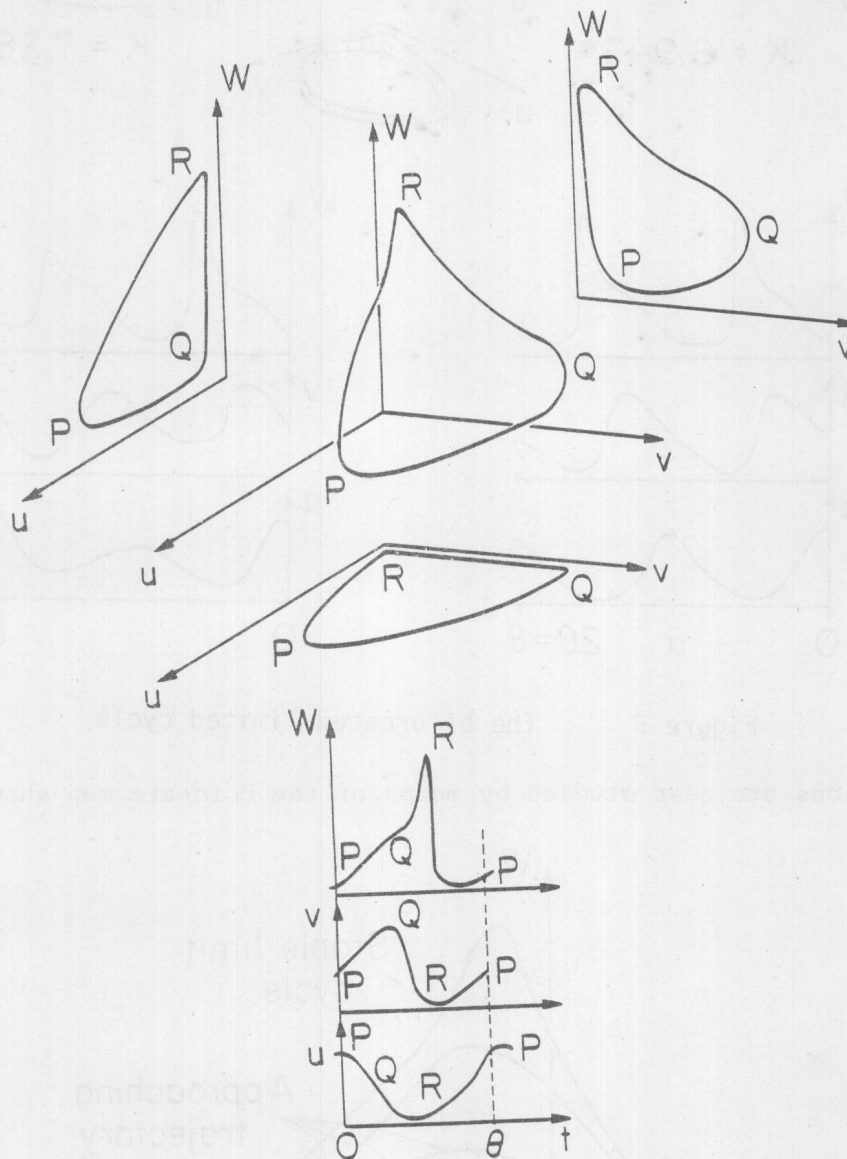


Figure 4 The basic limit cycle

from P to a point Q of maximum v quite close to the v,w-plane, swings up to a temperature maximum at R where A and B are virtually absent. However, there is then little reaction and the temperature falls while the concentration of A builds up and we are back at P starting the cycle again. The bottom of Fig. 4 shows u, v, and w as functions of time t over a period θ . The curves have been slightly distorted to avoid the extreme sharpness that is often observed and to bring out the essential qualitative features. As κ is increased the shape of the limit cycle varies and the period changes slightly until at $\kappa=6.949$ the single limit cycle is no longer stable. In its place the stable limit cycle for κ ever so slightly greater than this value is the limit cycle transversed twice instead of once. Further increase of κ peels these two strands apart into a loop of two distinguishable parts as shown in Fig. 5 until at $\kappa=7.283$ the double loop becomes quadrupled. This period doubling is so sufficiently important that it is worth turning aside to comment on in more detail.

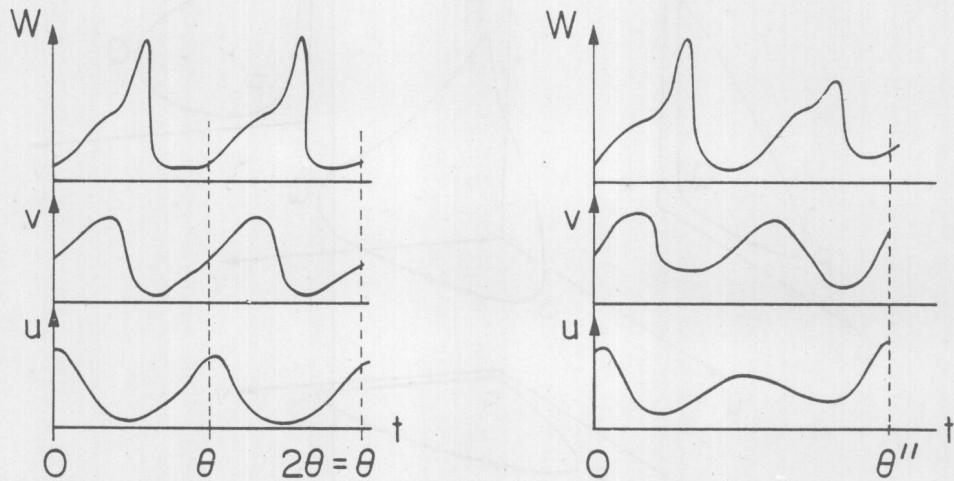
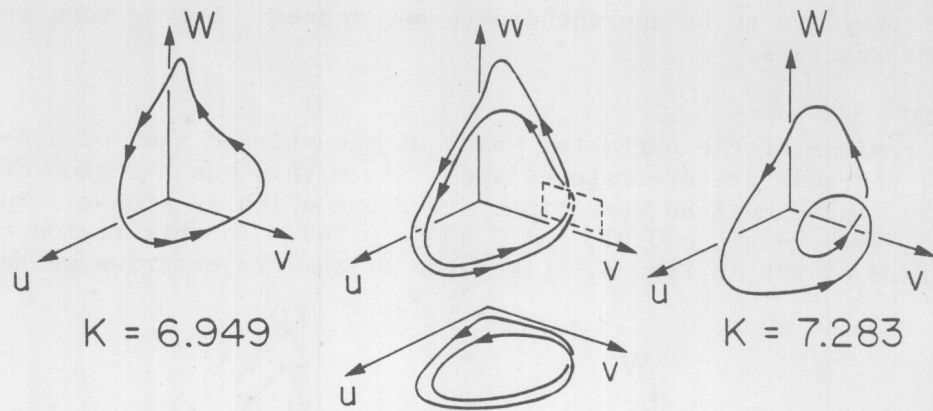


Figure 5 The bifurcated limited cycle

15. Periodic solutions are best studied by means of the Poincaré map shown in Fig. 6.

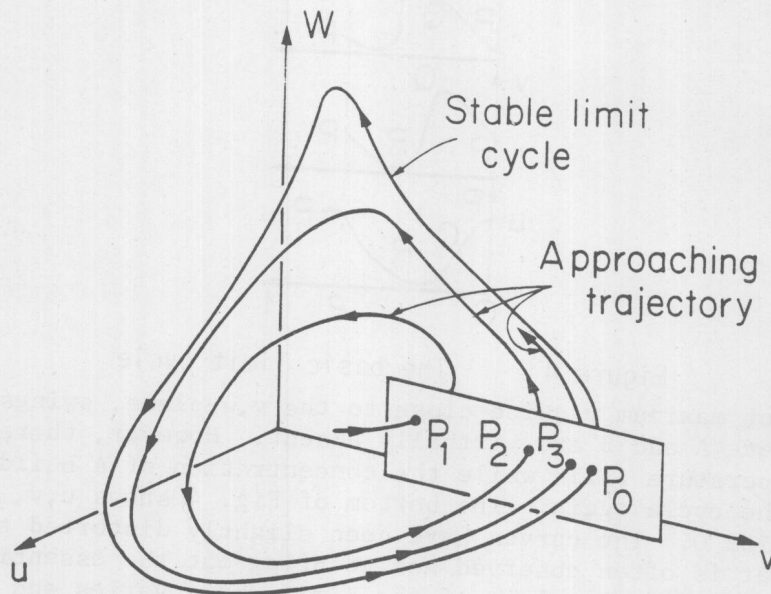


Figure 6 The Poincare map

If $P_0, (u_0, v_0, w_0), u_0 = u(t_0)$ etc., is a point of the limit cycle, a plane $l(u - u_0) + m(v - v_0) + n(w - w_0) = 0$ can be set up across the trajectory; the direction $l:m:n$ must not be normal to the trajectory and could, for definiteness, be taken tangentially. Since P_0 is on the limit cycle, the next time the solution point hits the plane (i.e. at $t_0 + \theta$, where θ is the period) at the same point P_0 , since $u(t_0 + \theta) = u(t_0)$, etc., defines a perio-

dic trajectory. If $P_1 = (u_1, v_1, w_1)$ is a point in the transverse plane near P_0 , the point P_2 at which the trajectory next penetrates the plane will not be the same as P_1 nor will the interval $(t_2 - t_1)$ between the times of penetration be exactly θ . However, if the limit cycle is stable and $P_1, P_2, P_3 \dots$ are successive points of penetration, then P_n will converge on P_0 and $(t_n - t_{n-1})$ will tend to θ . Thus P_0 is a fixed point of the return map of the transversal plane into itself, r , defined on a neighbourhood of P_0 by saying that any point is mapped into the next point on the trajectory which lies in the transversal plane. Clearly if r is a contraction mapping and $r(P_0) = P_0$ then the trajectory through P_0 is a stable limit cycle. This is the basis for the stability criterion of a limit cycle that the Floquet multipliers must lie in the unit circle.

16. We can now see how the period doubling occurs, for if P_0 loses its stability there may break away from it two points P'_0 and P''_0 such that $r(P'_0) = P''_0$ and $r(P''_0) = P'_0$, i.e. P'_0 and P''_0 are fixed points of the second return map $r_2(\cdot) = r(r(\cdot))$. If they are stable fixed points, the double loop is stable as in Fig. 5 where the central figure at the top indicates a possible transversal plane.

17. Though it is not the only route (cf. Refs. 18,19) to chaos, this successive period doubling is an important avenue (Refs. 20,21,22). Chaos is the name given to the situation when there is a solution which is neither periodic nor asymptotic to any periodic solution, and is evoking interest from all quarters these days (Ref. 23). The Poincaré map is not only a good indication of when this route is being taken, but may be used to suggest the existence of chaos by the Li-Yorke theorem (Ref. 24). This theorem states that when a continuous mapping of a line into itself produces a sequence of points $a \rightarrow b \rightarrow c \rightarrow d$ folded back on the line as $dabc$ or $cbad$, then there is a 'period 3' sequence, i.e. chaotic. Now the Poincaré map is frequently a segment of a line and by looking for sequences of return points folded back in this way, the existence of a truly chaotic system (i.e. not just one of very high periodicity) may be virtually established. I use the words 'suggest' and 'virtually establish', because it is not clear that the Poincaré map is truly of a line segment into itself. It may be a "thick line" or set of fractal dimension slightly greater than 1.

18. This technique was used by Jorgensen who found that the Poincaré return map was one dimensional as far as it was possible to judge. The existence of folded-back sequences was taken to be evidence of chaos and the trajectories were seen to wind around a rostrum in u, v, w -space (Ref. 15).

CONCLUSIONS

19. Space has only permitted us to look at one or two aspects of the dynamics of chemical reactors. Many other topics come under this heading and have been excellently surveyed by Hlaváček and Van Rompay (Ref. 25). The references given there must be consulted to supplement the few that can be given here within the limitations of space. What Luss and Balakotiah are doing for the multiplicity question needs to be carried forward to dynamical problems and an encouraging start has been made in the very penetrating analysis of Pismen (Ref. 26). Suffice it to say that there are problems enough and to spare that will afford problems of great interest for years to come. With the increasing availability of computers there arises a need, more pressing than ever, for thought.

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NOTATION

A_1, A_2	pre-exponential factors of rate constants
A_c	area of cooling surface
C_p	heat capacity per unit volume
c_A, c_B	concentrations of A and B
C_{Af}	feed concentration of A
$E(w)$	$\exp[\gamma w / (\gamma + w)]$
E_1, E_2	activation energies
P, Pi	points on return map
q	volumetric flow rate
R	gas constant
r	return map
T	temperature
\bar{T}	mean temperature $(T_f + \kappa T_c) / (1 + \kappa)$
T_c	coolant temperature
T_f	feed temperature
t', t	time, dimensionless time qt'/v
U	overall heat transfer coefficient
u, v	dimensionless concentrations of A and B
V	volume of reactor
w	dimensionless temperature
α	$(VA_1/q) \exp(-E_1/RT)$
β	$\{(-\Delta H_1)c_{Af}/C_p\} \gamma$
γ	E_1/RT
θ	period of oscillation
κ	VA_c/qC_p
ν	E_2/E_1
ρ	$\Delta H_2/\Delta H_1$
σ	$(A_2/A_1) \exp\{(E_1 - E_2)/RT\}$

REFERENCES

1. N.R. Amundson, paper in these proceedings.
2. N.R. Amundson, selected papers; "The mathematical understanding of chemical engineering systems" Pergamon Press, Oxford 1980.
3. R. Aris, "A note on the structure of the transient behaviour of chemical reactors" Chem. Eng. J. 1971, 2, 140.
4. N.R. Amundson and R. Aris, "An analysis of chemical reactor stability and control. Parts I-III" Chem. Engng. Sci. 1958, 7, 121.
5. N.R. Amundson and R.A. Schmitz "An analysis of chemical reactor stability and control, Part V" Chem. Engng. Sci. 1963, 18, 265.
6. G.R. Gavalas, "Nonlinear differential equations of chemically reacting systems" Springer Verlag, Heidelberg 1968.
7. A. Uppal, W.H. Ray and A.B. Poore, "On the dynamic behavior of continuous stirred tank reactors" Chem. Engng. Sci. 1974, 29, 967
8. A. Uppal, W.H. Ray and A.B. Poore, "The classification of the dynamic behavior of continuous stirred tank reactors--influence of reactor residence time" Chem. Engng. Sci. 1976, 31, 205.
9. D.A. Vaganov, N.G. Samoilenko and V.G. Abramov, "Periodic regimes of continuous stirred tank reactors" Chem. Engng. Sci. 1978, 33, 1133.
10. T.T. Tsotsis and V.K. Kwong "Fine structure of the CSTR parameter space" A.I.Ch.E.Jl. 1983, 29, 343, referring to a paper of the same title by D.C. Williams and J.M. Calo AIChEJl 1981, 27, 514.
11. N.R. Amundson and O. Bilous "Chemical reactor stability and sensitivity" A.I.Ch.E. Journal 1955, 1, 513.