## EFFECT OF CATALYST PORE BIZE JISTRZBUTTCA IN RESTDUE DESULFURISATION.

A Thesis<br>Presented to the Faculty of the Chemical Engineering Deparcment University of Houston Houston, Texas.

In Partial Fulfillment of the Requirements for the Derree of Master of Science

by<br>K.Rajagopalan<br>May, 1978

## ACKNOWLEDGEMENTS

I would like to express my thanks to Professor Dan Luss who helped and guided me throughout the course of this work. I an aiso thankful to the Department of Chemical Engineering, University of Houston, for providing the financial support. Special thanks are due to my collegues in the department, Stig Wedel, Pradip Mehta and S.Sundaresan for many helpful discussions.

# EFFECT OF CATALYST PORE SIZE DISTRIBUTION IN RESIDUE DESULFURISATION. 

An Abstract of a Thesis Presented to the Faculty of the Chemical Engineering Department University of Houston Houston, Texas.

In Partial Fulfillment of the Requirements for the Degree of Master of Science
by
K.Rajagopalan.

May, 1978


#### Abstract

During the hydrodesulfurisation of residuum oil, the metal corpounds present in the feed, deposit as sulfides on the catalyst pores, causing deactivation. The radius of the asphaltene molecules present in the residuum oil are of the same order as those of the catalyst pores. Diffusivity under such circumstances is influenced by the ratio of the molecular to pore radius. The intrinsic hydrodesulfurisation activity of the catalyst is proportional to the catalyst surface area. The presence of large pores result in a small catalyst surface area while small pores have large surface area and large resistance to diffusion. There is an intermediate pore size for optinal activity. Previous investigators of optimum pore size considered only initial catalyst activity. In the present work, numerical and analytical methods are used to follow deactivation due to pore plugging and optimisation is based on catalyst activity throughcut its life span. Algebroic expressions for optimum pore radius are developed for slab and spherical catalysts. The optimum pore size depends only on a single dimensionless group involving the rate constant, reactant diffusivity, the molecular radius and a characteristic catalyst dimension. At low and high values of Thiele Modulus, the optimum pore radius is shape independent. At intermediate values of Thiele Modulus the optimun pore radius for a spherical catalyst is larger than that for a slab.


The activity of the catalyst can be upproximated as a linear function of time for a wide range of Thiele Madulus. Expressions for the rate of deactivation were developed for slab and spherical catalysts. In both cases, the rate of deactivation is inversely related to the pore
radius, strongly influenced by the rate constant and weakly influenced by the reactant diffusivity.

Expressions were developed relating the activity of a catalyst with non-uniform pore size distribution to that of a catalyst with uniform pore size. Effect of plugging on catalysts with Gaussian, Gamma, Maxwell and Rayleigh distributions of pore volume were studied. The most desirable distribution is one with a small variance and with the HARMONIC MEAN pore radius equal to the optimal one.
Page

1. INTRODUCTION ..... 1
2. REVIEW OF PFEVIOUS WORK AND SCOPE OF PRESENT WORK
2.1 Kinetics of Hydrodesulfurization ..... 3
2.2 Previous Work on Modelling Pore Plugging ..... 8
2.3 Scope of Present Work ..... 15
3. DIFFUSION AND REACTION IN A SINGLE PORE
3.1 Introduction ..... 16
3.2 Mass Balance for a Single Pore ..... 16
3.3 Solution Strategy ..... 21
3.4 Methods of Solution ..... 23
3.5 Selection of Parameters ..... 27
4. STUDY OF A SLAB CATALYST PARTICLE
4.1 Reaction Rate in a Slab Catalyst ..... 29
4.2 Maximum Life of the Catalyst ..... 31
4.3 The Optimum Pore Radius from the Numerical Method ..... 32
4.4 Characteristics of Deactivation ..... 39
4.5 Analytical Expression for Optimum Pore Radius ..... 43
4.6 Farametric Study of Catalyst Performance ..... 57
Page
5. INFLUENCE OF CATALYST SHAPE ON ITS PERFORMANCE
5.1 Introduction ..... 64
5.2 Parallel Pore Model and Its Extension to Simulate Spherical Catalyst Plugging ..... 64
5.3 Comparisons Between Slab Catalyst and Spherical
Catalyst ..... 70
5.4 Expressions for Optimum Pore Radius ..... 75
5.5 Parametric Study of Catalyst Performance ..... 81
6. INFLUENCE OF PORE SIZE DISTRIBUTION ON PLUGGING RATE
6.1 Effect of Pore Size Distribution on Catalyst Activity ..... 84
6.2 Numerical Method to Follow Deactivation of a
Catalyst with Arbitrary Pore Size Distribution ..... 89
6.3 Adaptation of Standard Statistical Distribution to Represent Pore Volume Distribution ..... 94
6.4 Results ..... 98
7. CONCLUSION ..... 104
NOMENCLATURE ..... 107
BIBLIOGRAPHY ..... 1.11
APPENDIX ..... 113

## LIST OF FIGURES

Page
2.1 Schematic view of Asphaltene micelles and associated inter-micellar fluid ..... 4
2.2 Growth pǎtern or coke and metal Sulfide deposits ..... 7
2.3 Equilibrium Parcition Coefficient ..... 12
2.4 Derivation of molecular flux of large spherical particles involving configurational diffusion ..... 13
3.1 Mass Balance in a plugged pore ..... 17
3.2 Location of nodal points in finite difference calculation ..... 25
4.1 Maximum life variation with molecular radius ..... 33
4.2 Activity variation with plugging ..... 35
4.3 Comparison of pore sizes below the initial optimum ..... 36
4.4 Comparison of pore sizes above the initial optimum ..... 38
4.5 Time variation of reactant concentration at different positions in the catalyst ..... 42
4.6 Growth of Metal Sulfide deposit ..... 44
4.7 Deposit profile at different catalyst ages ..... 45
4.8 Concentration profile at different catalyst ages ..... 46
4.9 Cumulative activity of the catalyst ..... 53
4.10 Effect of assuming a linear deactivation ..... 54
4.11 The optimum pore radius from the analytical expression ..... 58
Page
4.12 The optimum pore radius from numerical method ..... 61
5.1 Comparison of slab and spherical catalysts ..... 72
5.2 Comparison of pore sizes in a spherical catalyst ..... 74
5.3 Optimum pore radius for spherical catalysts ..... 82
6.1 Discontinuity in rate function ..... 92
6.2 Effect of variance of Gamma distribution ..... 99
6.3 Effect of variance at constant harmonic mean ..... 101
6.4 Approximation for a bimodal Gamma distribution ..... 102

CHAPTER 1

## INTRODUCTION

Increasing attention has been recently directed to the processing of "residuum oil" - the fraction of the full range crude remaining after all the distillate is taken overhead. Environmental regulations regarding sulfur oxide emissions require removal of a high percentage of the sulphur content of the residuum fuel. The established method of sulfur removal [1] is trickle bed hydrodesulfurization (HDS). Here hydrogen and oil flow cocurrently over a fixed catalyst bed at elevated temperatures and pressures. The special problems associated with kydrodesulfurization of residuum oil are [2]
(i) residuum sulfur is more "refractory" - it is harder to remove than gasoline sulfur.
(ii) Presence of asphaltenes or pentene insolubles in residuum oil.
(iii) Presence of metals - mainly Vanadium and Nickel.

During catalytic hydrodesulfurization, apart from coke deposits caused by cracking, the organometallic constituents of the residuum oil (Vanadium, Nickel compounds) react with hydrogen sulfide to produce solid deposits of metal sulfide. These deposits plug the catalyst pores causing reduction in HDS activity due to loss of surface.

When the size of a diffusing molecule is comparable to the size of the pores, the diffusivity decreases with decreasing pore size and vanishes as pore size equals molecular size. This influence is known
as the configurational diffusion effect. A high percentage of the metals in the residuum oil are contained in the asphaltenes [13] which have molecular sizes ranging from $20-500 \dot{\AA}$ [2]. These sizes are of the same order of magnitude as the size of a pore. A pellet containing small pores will have a low HDS activity because of the resistance offered by small pores to diffusion. A pellet containing large pores will have a low activity because of the low specific surface area. A suitable intermediate pore size will obviously have the optimal activity.

The two important aspects in the performance of a HDS catalyst are its initial activity and its "stability", the rate at which the catalytic activity decays due to plugging. Spry and Sawyer [18] accounted for the configurational diffusion effects and determined a "relative pore radius" for optimum initial activity. However a catalyst with optimum initial activity may nct necessarily have optimal activity throughout its life span. To examine this point and to determine an optimal catalyst pore size based on both initial activity and stability we need to simulate the plugging process and its effect on the activity of catalysts with different pore size distributions. This has been done in this work.

## CHAPTER 2

## REVIEW OF PREVIOUS WORK AND SCOPE OF PRESENT WORK

### 2.1 Kinetics of Hydrodesulfurization

The amount of metal deposit on catalyst pores controls the life of the catalyst with regard to its HDS activity [4]. Therefore any investigation of catalyst activity and rate of deactivation of plugging should account for the transport of metal carrying compounds in the catalyst. This requires a good understanding of the chemistry and kinetics of hydrodesulfurization reactions.

Beuther et al. and others $[5,6,7,8$ \& 16] studied the kinetiss of various HDS reactions. The problem is by no means simple since the exact chemical content of crude oil is yet to be established. It has been observed [13] that about half the elements of the periodic table are present in the crude.Vanadium; nicke1, copper, sodium, calcium and iron are known to be present. Most metals are contained in the asphaltenes. These are complex molecules and considerable work has been done to determine their exact structure. Most studies indicate that the asphaltenes can be considered as miceller clusters of molecules [Fig. 2.1]. It is also believed [3] that the metals are buried in the asphaltenes as porphyrins or sandwich compounds. This conjecture has however been disputed by Larson et al. [13] who contends that only a fraction of the metals can possibly be complexed as porphyrins. Because of the complexity of the problem we need an idealisation to describe the metal deposition.


MM - CARBON CHAINS OR NAPHTHENIG SHEETS

- CONDENSED AROMATIC SHEETS

FIG 2.1 SCHEMATIC VIEW OF ASPHALTENE MICELLES
. AND ASSOCIATED INTER-MICELLER FLUID
(LARSON\& BEUTHER[13])

Vanadium and Nickel are present in significant quantities in the residuum fue1. Nickel is present in smaller quantities and is more difficult to remove than is Vanadium [13]. So a typical Vanadium bearing compound A may be used to represent the metal deposition in the catalyst. Desulfurization and metals deposition (demetallation) are two parallel reactions $[6,14]$.


The Vanadium removal reaction was found to be first order by Dautzenberg et al. [4]. This is because the hydrogen diffuses much faster than Vanadium containing compounds and can be considered to be available in excess. Evidence also exists $[15,16]$ that the parallel hydrodesulfurization reaction is of first order. The rate of hydrodesulfurization, therefore, is proportional to the rate of demetallation for the above reaction system. The above simplification of the chemistry and kinetics has also been adopted by previous investigators [4,11,18].

Coke deposits caused by cracking of residuum oil in a HDS catalyst may influence the plugging of the catalyst. Beuther and Schmid [5] observed that the coke content of the catalyst increased sharply to an equilibrium level in a short time of about 40 hours. It was postulated that this was due to a period of uncontrolled hydrocracking. Subsequently the coke content remained constant with processing time. The first 40 hours of coke deposits can be termed "fast coke" and subsequent
deposits can be termed "slow coke". The growth of coke and metal sulfide deposits in a typical desulfurization experiment is shown in Fig. 2.2 [Duntzenberg et al. (4)].

Beuther and Schmid [5] compared the physical properties of various HDS catalysts. By comparing surface areas and pore size distributions of fresh and spent catalysts, it was shown that the average pore radius was reduced only slightly and the pore size distribution remained almost the same after initial coking. This phenomenon was later confirmed by Oxenreiter et al. [17].

In this work, we simulate the activity of the catalyst after the fast coke deposition. Since the fast coke does not affect the pore size distribution significantly we can base our calculations on the initial pore size distribution, accounting for metal sulfide and slow coke deposits only. Thus we neglect the metal sulfide deposited during the fast coke deposition period. Newson [11] estimated the slow coke deposition to be $30 \%$ of metal sulfide deposition. Thus if the metal sulfide deposition rate is known the total deposit rate due to metal sulfide and slow coke can be got.

Another aspect of the kinetics of demetallation and desulfurization reactions is the effect of plugging on subsequent reaction rate at the site of plugging. It has been observed [19] that HDS activity of catalysts remain relatively unaffected even with significant amount of metal deposits. In this context, it is of interest to note the definitions of different types of pore plugging given by Hughes \& Mann [12]. They define poisoning as active site deactivation by monolayer type adsorption

at the site with no further poison adsorption taking place at that location. In this way, a great loss of activity can take place with the adsorption of very small amounts of poison. They define fouling as a phenomenon in which successive adsorption on the surface can take place such that significant amounts of material can accumulate. In this case physical blocking of the surface does take place but there is scope for further activity loss. Obviously plugging of the HDS catalyst takes place by the fouling mechanism. Previous investigators [4,11] assumed that plugging reduced activity only because of the reduction of surface area and there was no loss of active sites.

Commercial HDS reactions are carried out in downflow trickle bed or ebullated bed reactors. From process descriptions in pertinent literature [20] it is found that the ebullated bed reactor is backmixed and is approximately isothermal. The temperature difference between any two points in the reactor is less than $5^{\circ} \mathrm{F}$. Previous workers modelling the demetallation reaction $[4,11]$ have therefore used a single rate constant for the whole reactor.

### 2.2 Previous Work on Modelling Pore Plugging

Van Zoonen et al. [9] used different pelleting pressures to prepare catalysts of different pore size distributions. They conducted experiments on these catalysts and described the HDS reactor as a simple plug flow reactor. They concluded that pore size distribution affects the HDS activity and that a good catalyst must have both macropores (for good diffusivity) and micropores (for surface area). More specific conclusions
could not be reached because there was no basis for comparing catalysts of different pore size distributions. (For example, there wasn't a single group of catalysts with the same porosity, or the same specific surface area or the same mean diameter. All the parameters varied randomly among the catalysts tested). They also did not study the deactivation or stability of the various catalysts.

Hughes and Mann [12] proposed a theory for pore plugging systems that can be used to compare the stability of catalysts of different pore size distributions. They assumed that deposits on the pore have the shape of wedges. For a given slope of the wedge and amount of plugging they caiculated the ratio of the unplugged accessible area to the total area, for the catalyst of a given pore size distribution. For a kinetic controlled system the activity is related to the free area. They applied their results to the HDS system. Even if the HDS system is kinetic controlled at the start of the plugging it will become diffusion controlled as the pores get plugged because of the restricted diffusion of the bigger molecules. So the application of their model to the HDS system is doubtful. It can also be pointed out that their model requires use of an empirical poisoning parameter - the slope of the wedge.

Newson [10] assumed a conversion in the HDS reactor and an effectiveness of desulfurization and demetallation and predicted the approximate life of the catalyst. In a later work [11] he improved his methods to follow the catalyst deactivation for different pore size distributions. He assumed that the demetallation reaction was diffusion controlled and describable by first order kinetics. The weak points in his mathematical
modelling are - the assumption of uniform plugging when in reality higher concentration at the pore mouth causes preferential plugging; representation of a spherical catalyst by a system of parallel pores of the same length, and use of a time averaged effectiveness factor eventhough the catalytic activity and the effectiveness factor decay with time.

Dautzenberg et al. [4] did not assume uniform pore plugging but determined the deposit thickness profile. They assumed first order kinetics for demetallation and represented the spherical particle by a system of pores of the same length which is "very large". As the catalyst ages the outer surfaces of the catalyst gets extensively plugged relative to the interior of the catalyst. The free surface area inside the particle becomes virtually inaccessible to reactant molecules. Hence, in the study of pore plugging, the accessibility of the surface area is important. Averaging of pore length in a sphere means altering the prevailing accessibility of pore surfaces. Hence, when a spherical catalyst is modelled variations in pore length must be taken into account with a predicted pore structure.

Newson, in his earlier work [10] called for a mathematical approach that takes into account the reduction in diffusivity due to plugging. It is interesting to note that none of the above investigators have done that.

When the size of the diffusing molecules become greater than a tenth of the pore size, diffusion of the molecules will be "restricted" - [18] that is, diffusivity will decrease with decreasing pore diameter. The concept of steric limitation of large molecules in pores was first introduced by Ferry [21] in 1936. Referring to Fig. 2.3 a molecule with a
diameter $2 \sigma$ will be excluded from entering the pores if it approaches the pore wall any closer than $\sigma$. Thus the free area available to the molecule is shown by a dashed circle. Giddings [22] devised a steric partitioning coefficient to be $\phi=(1-\lambda)^{2}$ where $\lambda$ is a size ratio approximated by the ratio of the molecular radius to the pore radius. $\phi$ is the ratio of the cross sectional area of the dashed circle to the cross sectional area of the pore in Fig. 2.3.

In addition to this geometrical effect, Anderson \& Quinn [23] included a hydrodynamic effect as shown in Fig. 2.4. They assumed that spherical particles suspended in a solvent were moving down a cylindrical pore where the velocity could be described by an undisturbed Poiseville flow field. In addition the spherical particles were being transported by a diffusive flux as described by the Einstein equation. By combining the two flux terms, Anderson and Quinn developed the following type of expression for the net axial solute flux in the straight pore, which was modified [18] to account for tortuosity to give

$$
\begin{equation*}
\mathrm{N}_{\mathrm{A}}=\mathrm{K}^{-1} \frac{\mathrm{D}_{\mathrm{A}}}{\tau} \frac{\mathrm{dC}}{\mathrm{dz}}+\mathrm{GCV} \tag{2.2-1}
\end{equation*}
$$

where $K^{-1}$ is the reciprocal of the enhanced friction factor $(k=$ ratio of pore to bulk friction coefficient), G "the lag coefficient" accounting for the retarding effect of the pore wall and $V$ is the velocity as described by the Poiseville equation. The equation was then integrated over the cross section of the pore to give an average flux ( $\left(\bar{N}_{A}\right)$. The convective flux term of the average flux ( $\bar{N}_{A}$ ) could be neglected [18] for a catalyst pellet with a primary diffusive flux. Thus

1

$\phi=(1-\lambda)^{2} . \quad \lambda=\sigma / a$
FIG 2.3 EQUILIBRIUM PARTITION

4
COEFFICIENT. (FERRY[21])


$$
N_{A}=-K^{-1} \frac{D_{A}}{\tau} \frac{d C}{d Z}+G C V
$$

FIG 2.4 DERIVATION OF MOLECULAR FLUX. OF LARGE SPHERICAL PARTICLES INVOLVING CONFIGURATIONAL DIFFUSION [ANDERSON (23)]

$$
\begin{equation*}
N_{A}=-\xi \frac{\varepsilon D_{A}}{\tau} \frac{d C}{d z} \tag{2.2-2}
\end{equation*}
$$

where

$$
\begin{equation*}
\xi=\phi K^{-1}(\lambda) \tag{2.2-3}
\end{equation*}
$$

The average reciprocal enhanced friction factor $K^{-1}$ is a complicated expression and has not been evaluated for a porous pellet. However it can be approximated by the steric partitioning coefficient, $\phi[18]$. The following equation results.

$$
\begin{equation*}
\xi=\frac{\mathrm{D}_{\mathrm{e}}}{\varepsilon \mathrm{D}_{\mathrm{A}^{\prime} \tau}}=\phi \mathrm{k}^{-1} \simeq(1-\lambda)^{4}=(1-\sigma / a)^{4} \tag{2.2-4}
\end{equation*}
$$

Hence

$$
\begin{equation*}
\mathrm{D}_{\mathrm{e}}=\frac{\mathrm{D}_{\mathrm{A}}{ }^{\varepsilon}}{\tau}\left(1-\frac{\sigma}{\mathrm{a}}\right)^{4} \tag{2.2-5}
\end{equation*}
$$

The above equation reduces to the well known expression for effective diffusivity as molecular radius becomes negligible compared to the pore radius.

Spry and Sawyer [18] used the above model for configurational diffusivity to determine an optimum relative pore size. They made use of the standard expression for spherical particle effectiveness involving the Thiele Modulus which is good only for a fresh catalyst. As the catalyst gets plugged, effectiveness will be lower than that given by the standard expressions. The cptimann size obtained by Spry and Sawyer will only give optimum initial activity. A good catalyst should have both a high initial activity and a low rate of deactivation. To determine such an optimum, simulation of the plugging process and its effect on catalyst activity needs to be done. Dautzenberg et al. [4] and Newson [11]
developed methods of calculating the rate of deactivation. However both these investigators didn't take into account the effect of restricted diffusion.

### 2.3 Scope of Present Work

There is a need for an analysis that compares activity and stability of catalysts with different pore size distrilutions. This approach should eliminate the unnecessary assumptions of the previous works and take into account factors such as configurational diffusion, preferential plugging at the pore mouth and the "pore length distribution" in a spherical pellet. Such an approach has been attempted in the present work.

The quasi steady state plugging is determined by solving numerically for the diffusion and reaction in a plugged slab catalyst of uniform pore size. By comparing the activity time behavior of catalysts of different pore sizes, an optimal pore size can be established. An approximate expression for optimum pore size as a function of the Thiele Modulus is also developed. The numerical solution is extended to spherical pellets by integrating over a simulated length distribution using GaussianLegendre quadrature. Similar integration is done to predict the behavior in a catalyst of a given pore size distribution.

All the aspects of the plugging problem have been solved in the sense that if the reçuired parameters are known the concentration profile and the deposit profile in the catalyst as well as the rate of accumulation of the foulant can be determined apart from the life of the catalyst.

## CHAPTER 3

## DIFFUSION AND REACTION IN A SINGLE PORE

### 3.1 Introduction

The ebullated bed hydrodesulfurization reactor can be modelled as a well mixed reactor [4]. Results on the catalyst activity for a single particle can thus be a measure of activity in the whole reactor. As a first step in predicting reaction rate in a catalyst particle we analyse the behavior of a single pore of length $\ell$ and initial radius $a_{o}$. A slab catalyst of uniform pore size, a spherical catalyst of uniform pore size and a slab catalyst having a non-uniform pore size distribution can be expressed by a linear combination of pores of varying radius and length. Thus if the single pore problem is completely solved, the behavior of catalyst pellet of any shape can be predicted.

### 3.2 Mass Balance for a Single Pore

In catalyst pore the reactant concentration is maximum at the exterior surface of the catalyst and decreases with distance from the surface. Plugging will therefore be higher at the pore mouth than at the interior of the pore. At any arbitrary age $t$, let the shape of the pore be as shown in Fig. 3.1. We make the following assumptions.
(i) Plugging reduces surface area and increases resistance to diffusion. So the concentration profile in the catalyst changes with plugging. However plugging is a slow process. The time taken for significant changes in concentration and reaction rate is of the order of days.


FIG 3.1 MASS BALANCE IN A PLUGGED PORE

The concentration profile in the catalyst can be assumed to be in pseudo steady state. That is, rate of change of reactant concentration with time is negligibly small compared to the rate of change of concentration with position in the catalyst.
(ii) The reacting system is represented by a typical asphaltenic molecule A containing sulfur and Vanadium, reacting with hydrogen gas


Both parallel reactions follow first order kinetics.
(iii) Plugging reduces surface area but does not deactivate active sites.
(iv) The catalyst pellet is isothermal.
(v) The effect of fast coke on pore size distribution is neglected. Only slow coke and metal sulfide deposits are considered.

With these assumptions, the mass balance of a Vanadium bearing compound A is sufficient to describe the system. Noting that the "free pore radius" (got by subtracting the thickness of plugging from the initial pore radius) and hence effective diffusivity are functions of axial position, for the differential element of Fig. 3.1.

$$
\begin{equation*}
\frac{1}{a^{2}} \frac{d}{d z}\left(a^{2} D_{e} \frac{d C_{A}}{d z}\right)-k_{s} \cdot \frac{2}{a} C_{A}=0 \tag{3.2-1}
\end{equation*}
$$

with the boundary conditions

$$
\begin{equation*}
C_{A}=C_{A_{b}} \quad \text { at } z=0 \tag{3.2-2}
\end{equation*}
$$

$$
\begin{equation*}
\frac{\mathrm{dC}_{\mathrm{A}}}{\mathrm{dz}}=0 \quad \text { at } \mathrm{z}=\ell \tag{3.2-3}
\end{equation*}
$$

At time $t=0$, $D e \equiv D e_{o}$ and $a \equiv a_{0}$ for $a l l z$ and $D e_{o}$ and $a_{o}$ are known, we define the following dimensionless variables,

$$
\begin{align*}
f & =a / a_{o}  \tag{3.2-4}\\
g & =D e / D e_{o}  \tag{3.2-5}\\
\eta & =z / \ell  \tag{3.2-6}\\
\Psi_{A} & =C_{A} / C_{A_{b}} \tag{3.2-7}
\end{align*}
$$

The Thieles Modulus is defined as

$$
\begin{equation*}
\phi=\ell \sqrt{\frac{2 k_{s}}{a_{0} D e_{o}}} \tag{3.2-8}
\end{equation*}
$$

Equation (3.2-1) can be expressed in terms of the dimensionless variables as

$$
\begin{equation*}
\frac{1}{f^{2}} \frac{d}{d \eta}\left(f^{2} g \frac{d \psi_{A}}{d \eta}\right)-\frac{\phi^{2} \psi_{A}}{f}=0 \tag{3.2-9}
\end{equation*}
$$

The rate of the demetallion reaction $R$ in the single pore is given by

$$
\begin{align*}
R & =\int_{0}^{\ell} k_{s} C_{A} 2 \pi a \Delta z \\
& =k_{s} C_{A_{b}} 2 \pi a_{o} \ell \int_{0}^{1} \psi_{A} f d \eta  \tag{3.2-10}\\
& =k_{s} C_{A_{b}} 2 \pi a_{o} \ell \varepsilon
\end{align*}
$$

where $\quad \varepsilon=\int_{0}^{1} \psi_{A} f d \eta$ is the effectiveness factor which decreases with time due to plugging.

We know that the variables $f$ and $g$ are equal to one at time $t=0$. To predict their values for $t>0$ we need additional equations.

If $\alpha^{\prime}$ is the stiochiometric factor for the formation of metal sulfide, [that is, 1 mole of compound A leads to $\alpha^{\prime}$ moles of metal sulfide] $\alpha^{\prime} k_{S} C_{A}$ represents molar rate of deposition of metal sulfide per unit area. Let $\gamma$ be the ratio of the "slow coke" deposition rate to the demetallation rate. If the molecular weight of the deposit material is $M$,

$$
\begin{align*}
\frac{d m_{m}}{d t} & =(1+\gamma) \alpha^{\prime} k_{s} C_{A} M 2 \pi a \Delta s  \tag{3.2-11}\\
& =\alpha k_{s} C_{A} M 2 \pi a \Delta s \tag{3.2-12}
\end{align*}
$$

where $(1+\gamma) \alpha^{\prime}=\alpha$
For a deposit of thickness $\delta$

$$
\begin{equation*}
m_{m}=\rho_{m} \pi\left\{a_{o}^{2}-\left(a_{o}-\delta\right)^{2}\right\} \Delta s \tag{3.2-14}
\end{equation*}
$$

From equations (3.2-11) and (3.2-14) we get

$$
\begin{equation*}
\frac{d \delta}{d t}=\frac{M \alpha k_{s} C_{A}}{\rho_{m}} \psi_{A} \tag{3.2-15}
\end{equation*}
$$

Defining the dimensionless variable $\beta=\delta / a_{0}$

$$
\begin{equation*}
\frac{d B}{d t}=\left(\frac{M_{\alpha} k_{s} C_{A}}{a_{0} \rho_{m}}\right) \psi_{A} \quad \text { for } \quad 0 \leq \eta \leq 1 \tag{3.2-16}
\end{equation*}
$$

The above equation gives the rate of change of plug thickness as a function of position at any given time

$$
\begin{equation*}
\text { Obviously, } \quad f=1-\beta \tag{3.2-17}
\end{equation*}
$$

Plugging causes reduction of pore radius in relation to the molecular radius, resulting in a reduction of the effective diffusivity. This effect is represented by the variable $g$. From equation (2.2-5)

$$
\begin{equation*}
g=\left\{\frac{1-\sigma / a}{1-\sigma / a_{0}}\right\}^{4} \tag{3.2-18}
\end{equation*}
$$

(or) $\quad g=\left\{\frac{1-\frac{\lambda_{0}}{1-\beta}}{1-\lambda_{0}}\right\}^{4}$
The equations we need to solve can be grouped as

$$
\begin{array}{ll}
\frac{1}{f^{2}} \frac{d}{d \eta}\left(f^{2} g \frac{d \psi_{A}}{d \eta}\right)-\frac{\phi^{2} \psi_{A}}{f}=0 & \text { for } 0 \leq n \leq 1 ; ~ \\
\frac{d \geq 0}{d t}=\left(\frac{M \alpha k_{s} C_{b}}{a_{o} \rho_{m}}\right) \psi_{A} & \text { for } 0 \leq n \leq 1 ; t \geq 0 \\
f=1-\beta & \text { for } 0 \leq n \leq 1 ; t \geq 0 \\
g=\left(\frac{\left.1-\frac{\lambda_{0}}{1-\beta}\right)}{1-\lambda_{0}} 4\right. & \text { for } 0 \leq n \leq 1 ; t \geq 0 \tag{3.2-19}
\end{array}
$$

with the boundary conditions given by equations (3.2-2 \& 3).

### 3.3 Solution Strategy

The strategy of solving the system of equations is to solve the mass balance equation to determine the concentration profile and use that concentration profile to compute the variations of the dimensionless variables $f$ and $g$ from equations (3.2-16, $17 \& 19$ ). After these variations have been determined the mass balance equation (3.2-9) is solved again.

When carrying out the numerical calculations we have to determine a characteristic time of quasi steady state T. This is a time period during which changes in concentration and pore shape are so small that they can be considered to remain unchanged. Obviously, if the plugging is very slow, this characteristic time can be large. Since plugging and the resultant change of pore shape are the factors upsetting the quasi steady state, plugging accumulation at the pore mouth can be used to determine the characteristic time $T$. It can be postulated that the characteristic time is the time required to increase the dimensionJess plugging thickness at the pore mouth by a specified value $\beta_{\text {crit }}$, an increase which will upset the quasi steady state. During the characteristic time concentration and pore shape are unchanged Equation (3.2-16) can be easily integrated for the pore mouth $\left(\eta=0 ; \psi_{A}=1\right)$ to give

$$
\begin{equation*}
\beta_{\text {crit }}=\left(\frac{M_{s k}{ }_{s} A_{b}}{a_{o} \rho_{m}}\right) T \tag{3.3-1}
\end{equation*}
$$

$\beta_{\text {crit }}$ naturally depends on the desired accuracy. It was found that when time $T$ was chosen with $\beta_{\text {crit }} \leq 0.00369$ the computed concentration and deposit profiles were independent of the choice of $T$ up to four significant digits, so we selected

$$
\begin{equation*}
T=\frac{a_{o} \rho_{m}{ }^{\beta} \text { crit }}{M \alpha k_{s} C_{A_{b}}} \tag{3.3-2}
\end{equation*}
$$

with $\beta_{\text {crit }}=0.00369$

To initiate calculations equation (3.2-9) is solved with the initial conditions $f \equiv g \equiv 1$ and the resulting concentration profile used to determine the demetallation rate from equation (3.2-10). This rate is assumed to remain unchanged up to a time $T$. Given the characteristic time $T$ equation (3.2-16) can be easily integrated to give

$$
\begin{equation*}
\beta(t+T)=\beta(t)+\left(\frac{M \alpha k_{s} C_{A}}{a_{o} \rho_{m}}\right) \psi_{A} T \tag{3.3-4}
\end{equation*}
$$

$\beta(t=0) \equiv 0$. The above equation is used to compute $\beta(T)$ for $0 \leq n \leq 1$ and then equations (3.2-17 \& 19) are used to recompute $f$ and $g$. With these variations equation (3.2-9) is solved again to generate a new concentration profile valid for $T \leq t \leq 2 T$. The procedure is repeated to obtain the decay in activity with time. Equation (3.2-10) gives the demetallation activity at any time. The variable $f$ can be used to determine the deposit profile, the amount of metal accumulation as well as the life of the catalyst, as will be shown in the next chapter.

### 3.4 Methods of Solution

Equation (3.2-9) is solved numerically by a finite difference method. This equation can be written as

$$
\begin{equation*}
g\left(\frac{d^{2} \psi_{A}}{d n^{2}}\right)+\left(g^{\prime}+\frac{2 g f^{\prime}}{f}\right) \frac{d \psi_{A}}{d n}-\frac{\phi^{2} \psi_{A}}{f}=0 \tag{3.4-1}
\end{equation*}
$$

The corresponding difference equation is

$$
\begin{equation*}
g\left\{\frac{\psi_{A}(n-h)-2 \psi_{A}(n)+\psi_{A}(n+h)}{h^{2}}\right\}+\left(\frac{2 g f^{\prime}}{f}+g^{\prime}\right)\left\{\frac{\psi_{A}(n+h)-\psi_{A}(n)}{h}\right\}-\frac{\phi^{2} \psi_{A}(n)}{f}=0 \tag{3.4-2}
\end{equation*}
$$

which can be rearranged to give
$\psi_{A}(n+h)\left[g+\frac{2 g f^{\prime}}{f} h+g^{\prime} h\right]+\psi_{A}(\eta)\left[2 g+\frac{2 g f^{\prime}}{f} h+g^{\prime} h+\frac{\phi^{2} h^{2}}{f}+g \psi_{A}(\eta-h)=0\right.$
To use the finite difference method the pore is divided into twenty five equal parts. This means there are twenty six nodal points along the pore at which concentrations can be determined. These are shown in Fig. 3.2. Equation (3.4-3) can be written for the twenty five modal points - 2 to 26 . This will give us twenty five different equations. This will also introduce 27 unknowns $\psi_{A}(1)$ to $\psi_{A}(27)$. Nodal point 27 is immediately beyond the length of the pore. The no flux boundayy condition given by equation (3.2-3) can then be satisfied only if

$$
\begin{equation*}
\psi_{\mathrm{A}}(27)=\psi_{\mathrm{A}}(25) \tag{3.4-4}
\end{equation*}
$$

This also follows from the necessity of symmetry of concentration profile about the interior end of the pore.

From the other boundary condition given by equation (3.2-2);

$$
\begin{equation*}
\psi_{A}(1)=1 \tag{3.4-5}
\end{equation*}
$$

The above two equations have reduced the number of unknowns to twenty five viz. $\psi_{A}(2)$ to $\psi_{A}(26)$. The twenty five difference equations can be represented as

$$
\begin{equation*}
\overline{\overline{\mathrm{A}}} \bar{\psi}_{\mathrm{A}}=\overline{\mathrm{d}} \tag{3.4-6}
\end{equation*}
$$

where $\bar{\psi}_{A}$ is a column matrix containing the twenty five unknowns $\psi_{A}{ }^{(2)}$ to $\psi_{A}(26)$ and $\bar{A}$ is a $25 \times 25$ tridiagonal matrix.


FIG 3.2 LOCATION OF NODAL
POINTS IN FINITE DIFFERENCE
CALCULATION

$$
\overline{\bar{A}}=\left[\begin{array}{llllll}
a_{1} & b_{1} & & & &  \tag{3.4-7}\\
c_{2} & a_{2} & b_{2} & & & \\
& & c_{2} & a_{2} & b_{2} & \\
& & & c_{n-1} & a_{n-1} & b_{n-1} \\
& & & & c_{n} & a_{n}
\end{array}\right]
$$

with

$$
\begin{array}{lll}
a_{i}=-\left[2 g+\frac{2 g f^{\prime}}{f} h+g^{\prime} h+\frac{\phi^{2} h^{2}}{f}\right] & \text { for } & 1 \leq i \leq 25 \\
b_{i}=g+\frac{2 g f^{\prime}}{f}+g^{\prime} h & \text { for } & 1 \leq i \leq 24 \\
c_{i}=g & \text { for } & 2 \leq i \leq 24 \\
c_{25}=2 g+\frac{2 g f^{\prime}}{f} h+g^{\prime} h & & \tag{3.4-11}
\end{array}
$$

To evaluate $a_{i}, b_{i}, c_{i}$ for any $i$, the variables $f, g, f^{\prime}, g^{\prime}$ have to be evaluated at nodal position $i+1$. This is because, as i varies from 1 to 25 we evaluate concentration at nodal positions varying from 2 to 26.
$\overline{\mathrm{d}}$ in equation (3.4-6) is a column matrix with elements $\mathrm{d}_{1}$ to $\mathrm{d}_{25}$ such that

$$
\begin{equation*}
\mathrm{d}_{1}=-\mathrm{g} \tag{3.4-12}
\end{equation*}
$$

and

$$
\begin{equation*}
\mathrm{d}_{\mathrm{i}}=0 \quad \text { for } \quad \mathbf{i} \neq 1 \tag{3.4-13}
\end{equation*}
$$

The matrix system given by equation (3.4-6) is solved by the inversion of the Tridiagonal Matrix $\overline{\bar{A}}$ using the Thomas Algorithm. The details of this Algorithm are described in the Appendix. At tine $t=0, f \equiv g \equiv 1$ at all
positions and equation (3.2-9) can be solved analytically as

$$
\begin{equation*}
\psi_{\mathrm{A}}=\frac{\cosh [\phi(1-\eta)]}{\cosh [\phi]} \tag{3.4-14}
\end{equation*}
$$

The analytical solution is compared with the numerical solution obtained as above with the pore divided into twenty five parts. As long as the Thiele Modulus is not very large (for $\phi \leq 12$ ) the results are in agreement up to four significant digits. Thiele Modulus values greater than 12 represent cases of activity close to zero (for a given value of rate constant). They are also much higher than probable values of Thiele Modulus in HDS systems. So it is concluded that making twenty five finite divisions on the pore gives us a sufficient degree of accuracy.

Once equation (3.2-9) is solved by the above numerical method, the demetallation rate is obatined from equation (3.2-10). The numerical integration is carried out using the mid point rule, The concentration values calculated at the 26 nodal points are used in this integration.

### 3.5 Selection of Parameters

Some of the parameters needed for the calculation are difficult to determine. Hoog [16] pointed out that considerable differences in reaction velocity between the lighter and heavier sulfur compounds present in the oil prevent the calculation of an overall rate constant. However, estimates are available for some of the parameters such as diffusivity of the metal bearing compounds $[7,11]$ and the density of metal sulfide deposits,

The aim of this work is not the prediction of life of a given catalyst but only qualitative comparisons of performances of different catalyst pore size distributions. Most of the conclusions are fairly independent of the choice of the parameters. Even then, attempt has been made to make the most reasonable choice of the parameters. The intrinsic rate constant is chosen so that the life of the catalyst is comparable to that obtained in experiments. Whenever possible values reported in the literature are chosen. The effect of variations in uncertain parameters is also investigated.

## CHAPTER 4

## STUDY OF A SLAB CATALYST PARTICLE

In this chapter we examine the factors influencing the activity and deactivation of a slab catalyst. For simplicity a uniform pore radius is assumed. The influence of pore size distribution will be studied in a subsequent chapter. Commercial catalysts are not shaped like a slab. Hence in the next chapter shape effects on catalyst performance will be studied. Put together these will help us understand the plugging process in the HDS system with a view towards optimizing catalyst performance.

### 4.1 Reaction Rate in a Slab Catalyst

A slab catalyst can be modelled by a system of parallel pores of length equal to the product of the thickness $L_{\ell}$ of the slab and a tortuosity factor $\tau_{\ell}$. A slab of uniform pore size can hence be represented by a system of pores identical in radius and length. The number of pores n in a slab catalyst can be determined for a given initial porosity $\varepsilon$ from the relation

$$
\begin{align*}
\mathrm{nma}_{0}^{2} \mathrm{~L}_{\ell} \tau_{\ell} & =\varepsilon \mathrm{A}_{\ell} \mathrm{L}_{\ell}  \tag{4,1-1}\\
\mathrm{n} & =\frac{\varepsilon \mathrm{A}_{\ell}}{\pi \mathrm{a}_{0}^{2} \tau_{\ell}} \tag{4,1-2}
\end{align*}
$$

Let $\mathrm{S}_{\mathrm{g}}$ represent the specific surface area, $\mathrm{V}_{\mathrm{g}}$ the specific pore volume and $n_{g}$ the number of pores per gram of catalyst.

$$
\begin{aligned}
& S_{g}=n_{g} 2 \pi a_{o} L_{\ell} \tau_{\ell} \\
& V_{g}=n_{g} \pi a_{0}^{2} L_{\ell}{ }^{\tau} \ell
\end{aligned}
$$

which leads to

$$
\begin{equation*}
a_{o}=\frac{2 V_{g}}{S_{g}} \tag{4.1-3}
\end{equation*}
$$

The total pore surface area $S$ is a slab catalyst with face area $A_{\ell}$ is given by

$$
S=n 2 \pi a_{o} L_{\ell} \ell_{\ell}
$$

where $n$ is given by equation (4.1-2).
Hence

$$
\begin{equation*}
S=\frac{2 \varepsilon A_{\ell} L_{\ell}}{a_{0}} \tag{4.1-4}
\end{equation*}
$$

using equation (4.1-3)

$$
S=\frac{\varepsilon A_{\ell} L_{\ell} S_{g}}{V_{g}}
$$

From equation (4.1-4) it is evident that among catalysts of the same porosity, that with the smaller pore size has the larger surface area. Since the pores are parallel and nonintersecting the overall reaction rate $R_{\ell}$ in a slab catalyst is the rate $R$ in a single pore multipled by the number of pores in the catalyst as given by equation (4.1-2)

$$
\begin{equation*}
R_{\ell}=\frac{\varepsilon A_{\ell}}{\pi a_{o}^{2} \tau_{\ell}} \quad R \tag{4,1-5}
\end{equation*}
$$

While commercial catalysts vary widely in their specific surface area depending on catalyst pore size distribution, variations in porosity are
much less. The porosities of all commercial catalysts are in the range

$$
\begin{equation*}
\varepsilon=0.5 \pm 0.1 \tag{4.1-6}
\end{equation*}
$$

So it is reasonable to compare catalysts with the same porosity. Catalysts compared will have the same macroscopic dimensions and tortuosity (same $A_{\ell}$ and $\tau_{\ell}$ ). Hence from equation (4.1-5)

$$
\begin{equation*}
\mathrm{R}_{\ell} \propto \mathrm{R} / \pi \mathrm{a}_{\mathrm{o}}^{2} \tag{4.1-7}
\end{equation*}
$$

The above equation is used to calculate rates of demetallation in slab catalysts with different pore sizes. The demetallation rate in a single pore $R$ is calculated by the methods of Chapter 3 .

### 4.2 Maximum Life of the Catalyst

In a catalyst pore the reactant concentration is maximum at the pore mouth and decreases with distance from the pore mouth. Hence plugging is maximum at the pore mouth. As the pore mouth is plugged,diffusivity of reactant molecules drops due to increase in the ratio between the molecular radius and the pore radius. The diffusivity becomes zero when this ratio becomes one. At this time the catalyst will have lost its activity. The time required to plug the pore mouth so that $a=\sigma$ is the maximal life of the catalyst.

In a slab catalyst with uniform parallel pores, all the pores are identical and lose their activity at the same rate. The pore mouth concentration of the reactant is always equal to the bulk concentration. The time required to plug the pore mouth so that $a=\sigma$ (the thickness of plugging $\delta=a_{0}-\sigma$ ) can be determined from equation (3.2-16) as

$$
\begin{align*}
1-\lambda_{0} & =\left(\frac{\alpha k_{s} C_{A_{b}}^{M}}{a_{0} \rho_{m}}\right) t_{m \ell}  \tag{4.2-1}\\
t_{m \ell} & =\frac{\rho_{m}\left(a_{o}-\sigma\right)}{\alpha k_{s} C_{A_{b}}^{M}}  \tag{4.2-2}\\
t_{m \ell} & =\frac{\rho_{m} a_{0}\left(1-\sigma / a_{o}\right)}{\alpha k_{s} C_{A_{b}}^{M}} \tag{4.2-3}
\end{align*}
$$

The maximum life of a catalyst, therefore, is linear with molecular size and independent of diffusivity. The lack of dependence on diffusivity is because the maximum life is determined by pore mouth plugging where the concentration is the same as the bulk concentration regradless of the value of diffusivity. The variation of maximum life of a catalyst with molecular radius is shown in Fig. 4.1.

It should be noted that in reality, the life of a catalyst will be smaller than the maximum life defined in equation (4.2-2). This is because no catalyst is used to the point when its activity becomes zero and catalysts are replaced when activity becomes small compared to the initial activity.

### 4.3 The Optimun Pore Radius from the Numerical Method

The calculated initial activity of the slab catalyst for various pore sizes show an optimum pore size as observed earlier by Spry and Sawyer [18]. At low pore radii when the size of the reactant molecules is nearly the same as the pore size, the configurational diffusion effect is prominent and increase in pore size enhances the activity due to reduction

in resistance to diffusion. As pore size increases further, a stage is reached when configurational diffusion is no longer important and the reduction in specific surface area accompanying the increase in pore size causes a reduction in activity. Hence an optimum pore size exists. For pores smaller in size than this optimum, diffusion is the controlling factor. For pores larger in size than this optimum, kinetics is the controlling factor. The initial activity variation with pore radius for one specific choice of molecular radius is shown in Fig. 4.2 (curve for $t=0$ ). This shows an optimum pore radius of $25 \dot{A}$ for a molecule of radius $6.25 \dot{A}$.

As the catalyst ages, configurational diffusion becomes important even for larger pores which have a reduced "free" radius due to plugging. Hence the transition from diffusion control to kinetic control will occur at a larger pore size, It can be concluded that as the catalyst ages, the optimum shifts to larger pore sizes, This is shown in Fig. 4.2, The optimum determined by Spry and Sawyer [18] is the lowest of these series of optimum pore radii and is based only on initial activity, The actual optimum will be larger than this value, The optimum determined by Spry and Sawyer is a useful lower bound. To determine the actual optimum, the activity throug?out the catalyst life span has to be accounted for various pore sizes,

Fig. 4.3 compares demetallation activity decay wi.th time up to the maximum life of the catalyst, for catalysts with different pore radii below the initial optimum of $25 \dot{A}$. In this size range the larger pores


## FIG4.2 ACTIVITY VARIATION WITH PLUGGING



FIG 4.3 COMPARISON OF PORE SIZES BELOW THE INITIAL OPTIMUM
are always better than the smaller ones. Plugging decreases "free" radius and makes the configurational diffusion effect more pronounced. Hence the difference in activity between the larger and smaller pores increases with time.

For pore radii larger than $25 \dot{A}$, kinetics is the initial controlling factor. Catalysts with smaller pore size have a higher initial activity. The shift in the optimal pore radius to higher values causes the smaller pore sized catalysts to have a lower activity than the $1+$ ger pore sized catalysts as time progresses, This results in intersections, shown in Fig. 4,4, in the activity-time curves.

The cumulative activity of a catalyst throughout its life period can be determined from the area under the activity-time curve of Fig. 4,4. Comparison of catalysts of different pore sizes is complicated by the fact that they have different values of maximum life. A criteria needs to be established to compare catalysts.

In most applications there is a limiting desulfurization rate beyond which it is not practical to use the catalyst, A catalyst life can be defined to have ended when the activity falls below this value, Once this limiting activity is established the area under the activity-time curve up to this activity value can be compared for catalysts with different pore sizes to establish an optimum pore size. For the same set of pore sizes, the activity varies with the choice of the rate constant, initial diffusivity and other parameters. There needs to be a criterion for limiting activity which is suitable for all choices of


FIG4.4 COMPARISON OF PORE SIZES ABOVE THE INITIAL OPTIMUM
parameters. We cannot choose a single arbitrary limiting activity. A limiting activity that depends on the choice of the rate constant and other parameters is more appropriate.

When comparing catalysts with different pore sizes, the four key parameters are initial diffusivity, rate constant, molecular radius and bulk concentration. For a given set of these parameters there exists a maximum initial activity corresponding to an optimum initial pore size (for example, see Fig. 4.2). The activity of any catalyst at any time cannot exceed this value. An activity which is a fraction $F$ of the maximum initial activity can be chosen as the limiting activity. If the catalyst activity falls below this value it has to be replaced. The maximum initial activity and hence the limiting activity depend on the choice of rate constant and other parameters and have to be determined in each case. In Fig. 4.4, a limiting activity which is a quarter of the maximum initial activity is shown by a dotted line. The areas under the activity curve for different catalysts till they reach the limiting activity are compared in the insert of Fig, 4.4. An optimum pore radius of $46 \dot{A}$ is established.

A generalized method of expressing the optimal pore size is to express it in relation to the molecular size. An optimum pore radius of $46 \dot{A}$ is 7,36 times the molecular radius of $6,25 \dot{A}$.

### 4.4 Characteristics of Deactivation

Dautzenberg et al. [4] measured deactivation in a HDS reactor for various temperatures, flow velocities and other parameters. They defined
the time varying effectiveness of demetallation $E$ as the ratio of the demetallation activity of an aged catalyst to the activity of a fresh catalyst.

$$
\begin{equation*}
E=\frac{R_{\ell}(t)}{R_{\ell}(0)} \tag{4.4-1}
\end{equation*}
$$

Their theoretical and experimental results suggest that when the amount of plugging is not high (pore mouth plugged to less than $50 \%$ ) the effectiveness of demetallation varies linearly with pore mouth plug thickness.

$$
\begin{equation*}
E \propto E(a t \quad \eta=0) \tag{4.4-2}
\end{equation*}
$$

For a given system (fixed $k, D_{e}, a_{0}$ ) the activity of the fresh catalyst $R_{\ell}(0)$ is fixed and hence the effectiveness of demetallation (equation 4.4-1) is proportional to the time variant demetallation activity.
(i.e.) $E \propto R_{\ell}(t)$

At $\eta=0, \psi_{A}=1$ for all $t$ and from equation (3.2-16)

$$
\begin{equation*}
\beta(a t \quad \eta=0) \propto t \tag{4,4-4}
\end{equation*}
$$

From equations (4.4-2, $3 \& 4$ )

$$
\begin{equation*}
R_{\ell}(t) \propto t \tag{4,4-5}
\end{equation*}
$$

That is the demetallation activity is linear with time. Inspection of activity time curves of Fig. 4.4 show that linearity is a good approximation in the initial phase of the catalyst life.

The expression for rate of reaction in a catalyst pore was given in Section 3.2

$$
\begin{equation*}
R=k_{s} C_{A_{b}} 2 \pi a_{o} \ell \int_{o}^{1} \psi_{A} f d \eta \tag{3.2-10}
\end{equation*}
$$

Deactivation due to plugging is caused by two factors:
(i) reduction of free radius and surface area - (i.e.) reduction in the value of f in equation (3.2-10),
(ii) reduction in reactant concentration throughout the catalyst caused by increased resistance to diffusion - (i,e.) reduction in the value of $\psi_{A}$ in equation (3.2-10),

The surface area of the catalyst is proportional to the free pore radius. When the catalyst activity is kinetic controlled reactant concentration at any position in the catalyst is the same as the bulk concentration and concentration changes very slowly with time. The growth of metal sulfide deposit under constant concentration condition in linear with time [see equation (3,2-16)],

The surface area effect in linear with time and the concentration effect is negligible. The overall deactivation is hence linear.

When configurational diffusion controls the activity reactant concentration at positions inside the catalyst drop rapidly to low values. Metal sulfide deposits at these low concentrations are insignificant. Hence in the case of diffusion control surface area effect is significant and deactivation is caused by the concentration effect. The variation of the dimensionless reactant concentration with time at various positions in the catalyst is shown in Fig. 4,5. At high catalyst ages (in the region of diffusion control) the concentration change with time is found to be

linear. Hence in the diffusion controlled region surface area effect is negligible and concentration effect is linear. The overall deactivation is hence linear. This explains the approximately linear deactivation rate observed in Fig, 4.4.

The growth of metal sulfide deposit at various positions in the catalyst are shown in Fig, 4.6. The growth is steady near the external surface ( $\eta=0$ ) where the concentration is constant. Near the centre of the catalyst $\left(r_{1}=1\right)$ the deposits grow steadily for some time and then saturate, The saturation is caused by the rapid decline of concentration near the centre of the catalyst due to configurational diffusion effects.

Fig. 4.7 shows the deposit profile - the variation of the dimensionless plug thickness across the catalyst for various catalyst ages. The deposit grows at a constant rate near the catalyst surface and at a decreasing rate at interior points in the catalyst. The concentration profiles in the catalyst at various stages in catalyst life are shown in Fig. 4.8, It can be seen that the shape of the concentration profile is unaffected due to plugging.

### 4.5 Analytical Expression for Optimum Pore Radius

An expression for the optimum catalyst pore radius will be developed based on the approximation that the catalyst deactivates linearly with time.

## 4.5-1 Optimization of Initial Activity

It has been shown that the reaction rate $R_{\ell}$ in a slab catalyst of face area $A_{Q}$ is related to the reaction rate $R$ in a single pore by


## FIG 4.6 GROWTH OF METAL SULFIDE DEPOSIT



FIG 4.7 DEPOSIT PROFILE AT DIFFERENT CATALYST AGES


$$
\begin{equation*}
R_{\ell}=\frac{\varepsilon A_{\ell}}{\pi a_{o}^{2} \tau_{\ell}} R \tag{4.1-5}
\end{equation*}
$$

In the initial phase of the plugging the rate $R$ in a pore can be expressed in terms of the effectiveness factor.

$$
\begin{equation*}
R=k_{s} C_{A_{b}} 2 \pi a_{o} L_{\ell}{ }_{l}{ }^{\eta} \tag{4,5-1}
\end{equation*}
$$

The effectiveness $\eta$ for a single pore is

$$
\begin{equation*}
\eta=\frac{\tanh (\phi)}{\phi} \tag{4.5-2}
\end{equation*}
$$

where $\phi$ is the Thiele Modulus as given by

$$
\begin{equation*}
\phi=\tau_{\ell} L_{\ell} \sqrt{\frac{2 k_{s}}{a_{0} E_{e_{0}}}} \tag{4.5-3}
\end{equation*}
$$

Using equation (4,5-1) in equation (4.1-5) we can write

$$
\begin{equation*}
R_{\ell}=\frac{2 k_{s} C_{A_{b}}{ }^{\varepsilon A_{\ell} L_{\ell} \eta}}{a_{0}} \tag{4.5-4}
\end{equation*}
$$

Since $\quad \lambda_{0}=\sigma / a_{0}$

$$
\begin{align*}
& R_{\ell}=\left(\frac{2 k_{s} C_{A_{b}}{ }^{\varepsilon A_{\ell} L_{\ell}}}{\sigma}\right) \lambda_{o} \eta  \tag{4,5-6}\\
& R_{\ell}=C_{1} \lambda_{o} \eta
\end{align*}
$$

with

$$
\begin{equation*}
C_{1}=\left(\frac{2 k_{s} C_{A_{b}}^{\varepsilon A^{1}} \ell_{\ell}{ }^{L_{\ell}}}{\sigma}\right) \tag{4,5-7}
\end{equation*}
$$

$C_{1}$ being a constant for a given system the product $\lambda_{o} \eta$ has to be optimized for optimum initial activity

$$
\begin{equation*}
\frac{d}{d \lambda_{0}}\left(\lambda_{0} n\right)=0 \tag{4,5-9}
\end{equation*}
$$

$$
\begin{equation*}
\lambda_{0} \eta^{\prime}+\eta=0 \tag{4.5-10}
\end{equation*}
$$

Dividing throughout by $\eta$

$$
\begin{align*}
& \frac{\mathrm{d} \ell n \eta}{\mathrm{~d} \ln \lambda_{0}}+1=0  \tag{4.5-11}\\
& \frac{\mathrm{~d} \ell n \eta}{\mathrm{~d} \ln \phi} \cdot \frac{\mathrm{~d} \ell n \phi}{\mathrm{~d} \ell n \lambda_{0}}+1=0 \tag{4.5-12}
\end{align*}
$$

using equation (4.5-2)

$$
\begin{align*}
\frac{\mathrm{d} \ln \eta}{\mathrm{~d} \ln \phi} & =\frac{\mathrm{d} \ln [\tanh (\phi)]}{\mathrm{d} \ln \phi}-1 \\
& =\frac{\phi}{\tanh \phi} \frac{\mathrm{d} \tanh \phi}{\mathrm{~d} \phi}-1 \\
& =\frac{\phi \operatorname{sech}^{2} \phi}{\tanh \phi}-1 \\
& =\frac{\phi}{\sinh \phi \cosh \phi}-1 \\
& =\frac{2 \phi}{\sinh (2 \phi)}-1 \tag{4.5-13}
\end{align*}
$$

In general the initial effective diffusivity of the reactant can be expressed as

$$
\begin{equation*}
D_{e_{0}}=\frac{D_{A} \varepsilon}{\tau_{\ell}} f\left(\lambda_{o}\right) \tag{4,5-14}
\end{equation*}
$$

Equation (2,2-5) can be obtained for

$$
\begin{equation*}
f\left(\lambda_{0}\right)=\left(1-\lambda_{0}\right)^{4} \tag{4.5-15}
\end{equation*}
$$

Using equations (4.5-14) and (4,5-5), the Thiele Modulus as given by equation (4.5-3) can be written as

$$
\begin{equation*}
\phi=\tau_{\ell} L_{\ell} \sqrt{\frac{2 k_{s} \tau^{2}}{D_{A} \varepsilon \sigma}} \sqrt{\frac{\lambda_{0}}{f\left(\lambda_{0}\right)}} \quad \phi=\tilde{\phi} \sqrt{\frac{\lambda_{0}}{f\left(\lambda_{0}\right)}} \tag{4,5-16}
\end{equation*}
$$

where

$$
\begin{align*}
& \tilde{\phi}=\tau_{\ell} L_{\ell} \sqrt{\frac{2 k_{s}{ }^{\tau} \ell}{D_{A}{ }^{\varepsilon \sigma}}}  \tag{4.5-17}\\
& \begin{aligned}
\frac{d \ln \phi}{d \ln \lambda_{o}} & =\frac{1}{2}-\frac{1}{2} \frac{d \operatorname{lnf}\left(\lambda_{o}\right)}{d \operatorname{dnn} \lambda_{o}} \\
& =\frac{1}{2}-\frac{1}{2} \frac{\lambda_{0} f^{\prime}}{f}
\end{aligned}
\end{align*}
$$

From equations (4.5-12, 13 \& 19)

$$
\begin{equation*}
\left(\frac{1}{2}-\frac{\lambda_{0}}{2} \frac{f^{\prime}}{f}\right)\left(1-\frac{2 \phi}{\sinh (2 \phi)}\right)=1 \tag{4.5-19}
\end{equation*}
$$

The Thiele Modulus $\phi$ can be expressed in terms of $\tilde{\phi}$ and $\lambda_{0}$ by equation $(4,5-16)$. For a given value of the dimensionless group $\tilde{\phi}$ the above equation can be solved for the relative pore size $\lambda_{i}$ that corresponds to optimum initial activity.

Thus $\lambda_{i}=F(\tilde{\phi}$ oniy $)$.
The above equation is the general relation for ortimum pore size for any form of the function $f$.

When $f=\left(1-\lambda_{0}\right)^{4}$ equation (4.5-19) becomes

$$
\begin{equation*}
\left[1-\frac{2 \phi}{\sinh (2 \phi)}\right] \frac{\left(1+3 \lambda_{0}\right)}{2\left(1-\lambda_{0}\right)}=1 . \tag{4.5-20}
\end{equation*}
$$

For large values of Thiele Modulus

$$
\begin{aligned}
& \frac{2 \phi}{\sinh (2 \phi)} \rightarrow 0 \\
& \frac{1+3 \lambda_{0}}{2\left(1-\lambda_{0}\right)} \rightarrow 1
\end{aligned}
$$

If $\lambda_{i}$ is the optimum relative pore size that obeys the above equation

$$
\begin{equation*}
\lambda_{i}=1 / 5 \tag{4.5-21}
\end{equation*}
$$

It can be seen from equation (4.5-20) that for smaller values of the Thiele Modulus, $\lambda_{i}$ will be greater than the above value. Hence

$$
\begin{equation*}
1 / \lambda_{i}=\frac{a_{o}}{\sigma} \leq 5 \tag{4,5-22}
\end{equation*}
$$

If we want to optimize the initial activity of the catalyst the pore radius should be five times the molecular radius for a system with a high value of Thiele Modulus, Otherwise the pore radius should be less than five times the molecular radius.

The calculated initial optimum pore radius in Fig. 4.2 is $25 \dot{i}$ for a molecular radius of $6,25 \dot{A}$. In this case the Thiele Modulus is not high enough and the optimum pore radius is four times the molecular radius.

The optimization of catalyst pore size should take into account the activity of a catalyst throughout its life span. This is done in the next section.

## 4.5-2 Optimization of Overall Activity

The area under the activity time curve represents the overall activity of the catalyst. A catalyst has to be replaced when its activity falls below a limiting activity $\mathrm{C}_{3}$. The limiting activity can be chosen to be a fraction F of the optimum initial activity. The limiting activity $\mathrm{C}_{3}$ can be determined for a given set of kinetic and transport parameters and is a constant when catalysts of different pore radii are compared,

$$
\begin{equation*}
C_{3}=C_{1} \lambda_{i} \eta_{i} F \tag{4.5-23}
\end{equation*}
$$

where $F$ is less than or equal to one. The extent to which the user makes use of the catalyst decides the choice of $F$. Low values of $F$ imply that the catalyst will be used for a longer period of time before being replaced.

In equation (4.5-23) $\lambda_{i}$ is determined by solving equation (4.5-19) and $\eta_{i}$ the effectiveness factor corresponding to optimum initial activity, obtained from

$$
\phi_{i}=\tilde{\phi} \sqrt{\frac{\lambda_{i}}{f\left(\lambda_{i}\right)}}
$$

and

$$
\begin{equation*}
\eta_{i}=\frac{\tanh \left(\phi_{i}\right)}{\phi_{i}} \tag{4,5-24}
\end{equation*}
$$

In section 4.2 we showed that the catalyst activity vanishes when $t=t_{m l}$ as given by

$$
\begin{align*}
t_{m \ell} & =\frac{\rho_{m} a_{o}\left(1-\lambda_{o}\right)}{\alpha k_{s} C_{A_{b}}^{M}}  \tag{4.2-3}\\
& =\frac{\rho_{m} \sigma}{\alpha k_{s} C_{A_{b}}} \frac{1}{\lambda_{o}}\left(1-\lambda_{o}\right) \\
& =\frac{C_{2}}{\lambda_{o}}\left(1-\lambda_{o}\right) \tag{4,5-25}
\end{align*}
$$

where

$$
\begin{equation*}
C_{2}=\frac{\rho_{m}{ }^{\sigma}}{\alpha k_{s} C_{b}{ }_{b}^{M}} \tag{4,5-26}
\end{equation*}
$$

The activity falls from $C_{1} \lambda_{o} \eta$ to zero in a time $t_{m \ell}$. The linear rate of deactivation is therefore given by

$$
\begin{equation*}
-\frac{\mathrm{dR}_{\ell}}{\mathrm{dt}}=\frac{\mathrm{C}_{1} \lambda_{0} \eta}{\frac{\mathrm{C}_{2}}{\lambda_{0}}\left(1-\lambda_{0}\right)} \tag{4.5-27}
\end{equation*}
$$

The area under the activity time curve up to the limiting activity is the area of a right angled triangle (see Fig. 4,9), The vertical side of the right angled triangle is the difference between the initial activity $C_{1} \lambda_{0} \eta$ and the 1 imiting activity $C_{3}$. The horizontal side of the right angled triangle is the life of the catalyst $t_{\ell}$ which is the time taken for the catalyst activity to decrease to the limiting activity. The life of the catalyst $t_{\ell}$ can be found from the rate of deactivation given by equation (4, 5-27),

$$
\begin{equation*}
t_{\ell}=\frac{C_{2}\left(1-\lambda_{0}\right)}{\lambda_{0}\left(C_{1} \lambda_{0} n\right)}\left(C_{1} \lambda_{o} \eta-C_{3}\right) \tag{4.5-28}
\end{equation*}
$$

The area $\bar{A}$ of the right angled triangle the quantity to be optimized is given by

$$
\begin{equation*}
\bar{A}=\frac{C_{2}\left(1-\lambda_{0}\right)}{2 C_{1} \lambda_{0}^{2} \eta}\left(C_{1} \lambda_{0} \eta-C_{3}\right)^{2} \tag{4.5-29}
\end{equation*}
$$

Thus $\quad \bar{A} \propto \frac{\left(1-\lambda_{0}\right)\left(\lambda_{0} n-C_{3} / C_{1}\right)^{2}}{\lambda_{0}^{2} n}$
The validaty of the assumption of linear deactivation is tested in Fig. 4.10 where the actual activity time curve calculated numerically by the methods of Chapter 3 is compared with the approximated activity time



FIG 4.10 EFFECT OF ASSUMING A
LINEAR DEACTIVATION
curve obtained assuming linear deactivation. It can be seen that the areas under the two curves are quite close to each other.

In equation (4.5-30) the derivative $D_{1}$ of the numerator with respect to $\lambda_{0}$ is given by

$$
\begin{aligned}
& D_{1}=\left(1-\lambda_{0}\right) 2\left(\lambda_{0} \eta-\frac{C_{3}}{C_{1}}\right) \frac{d}{d \lambda_{0}}\left(\lambda_{0} \eta\right)-\left(\lambda_{0} \eta-\frac{C_{3}}{C_{1}}\right)^{2} \\
& \frac{d}{d \lambda_{0}}\left(\lambda_{0} \eta\right)=\lambda_{0} \eta^{\prime}+\eta \\
& \\
& =n\left(\frac{d \ln \eta}{d \ln \lambda_{0}}+1\right)
\end{aligned}
$$

using equations (4.5-12, 13 \& 18)

$$
\begin{equation*}
\frac{d}{d \lambda_{0}}\left(\lambda_{0} n\right)=n\left[1+\left(\frac{2 \phi}{\sinh (2 \phi)}-1\right)\left(\frac{1}{2}+\frac{\lambda_{0} f^{\prime}}{2 f}\right)\right] \tag{4.5-32}
\end{equation*}
$$

Hence

$$
\begin{equation*}
D_{1}=2\left(1-\lambda_{0}\right)\left(\lambda_{0} n-\frac{C_{3}}{C_{1}}\right) n\left[1+\left(\frac{2 \phi}{\sinh (2 \phi)}-1\right)\left(\frac{1}{2}-\frac{\lambda_{o} f^{\prime}}{2 f}\right)\right]-\left(\lambda_{0} n-\frac{C_{3}}{C_{1}}\right)^{2} \tag{4.5-33}
\end{equation*}
$$

In equation (4.5-20) the derivative $D_{2}$ of the denominator with respect to $\lambda_{0}$ is given by

$$
\begin{aligned}
D_{2} & =\frac{d}{d \lambda_{0}}\left(\lambda_{o}^{2} n\right) \\
& =\lambda_{o}^{2} \eta^{\prime}+n 2 \lambda_{o} \\
& =\lambda_{o} \dot{n}\left\{\frac{\lambda_{0} \eta^{\prime}}{n}+2\right\} \\
& =\lambda_{o} \dot{n}\left\{2+\frac{d \ln \eta}{d \ell n \lambda_{o}}\right\}
\end{aligned}
$$

Using equation (4.5-12, $13 \& 18$ )

$$
\begin{equation*}
D_{2}=\lambda_{0} n\left\{2+\left(\frac{2 \phi}{\sinh (2 \phi)}-1\right)\left(\frac{1}{2}-\frac{\lambda_{0} f^{\prime}}{2 \bar{f}^{\prime}}\right)\right] \tag{4.5-34}
\end{equation*}
$$

For optimum pore radius

$$
\begin{equation*}
\frac{\mathrm{d} \overline{\mathrm{~A}}}{\mathrm{~d} \lambda_{\mathrm{o}}}=0 \tag{4.5-35}
\end{equation*}
$$

Hence

$$
\begin{equation*}
\lambda_{0}^{2} n D_{1}=\left(1-\lambda_{0}\right)\left(\lambda_{0} n-\frac{C_{3}}{C_{1}}\right)^{2} D_{2} \tag{4.5-36}
\end{equation*}
$$

Substituting the expressions for $D_{1}$ and $D_{2}$ and simplifying

$$
\begin{gather*}
\lambda_{0}\left\{2\left(1-\lambda_{0}\right) n\left[1+\left(\frac{2 \phi}{\sinh (2 \phi)}-1\right)\left(\frac{1}{2}-\frac{\lambda_{o} f^{\prime}}{2 f}\right)\right]-\left(\lambda_{0} \eta-\frac{C_{3}}{C_{1}}\right)\right\} \\
=\left(1-\lambda_{0}\right)\left(\lambda_{0} \eta-\frac{C_{3}}{C_{1}}\right)\left[2+\left(\frac{2 \phi}{\sinh (2 \phi)}-1\right)\left(\frac{1}{2}-\frac{\lambda_{0} f^{\prime}}{2 f}\right)\right] \tag{4.5-37}
\end{gather*}
$$

The optimum relative pore size $\lambda_{\text {opt }}$ should satisfy the above equation. $C_{3} / C_{1}$ is a constant given by equation (4.5-23), The Thiele Modulus $\phi$ and the effectiveness factor $n$ can be expressed in terms of $\lambda_{0}$ (equations (4.5-16 \& 2) respectively). Given the function $f$, equation (4.5-37) can be solved for $\lambda_{\text {opt }}$. When $f=\left(1-\lambda_{0}\right)^{4}$ equation (4.5-37) becomes

$$
\begin{gather*}
\lambda_{0}\left\{2\left(1-\lambda_{0}\right) n\left[1+\left(\frac{2 \phi}{\sinh (2 \phi)}-1\right)\left(\frac{1+3 \lambda_{0}}{2\left(1-\lambda_{0}\right)}\right)\right]-\left(\lambda_{0} \eta-\frac{C_{3}}{C_{1}}\right)\right\} \\
=\left(1-\lambda_{0}\right)\left(\lambda_{0} \eta-\frac{C_{3}}{C_{1}}\right)\left[2+\left(\frac{2 \phi}{\sinh 2 \phi}-1\right)\left(\frac{1+3 \lambda_{o}}{2\left(1-\lambda_{0}\right)}\right)\right] \tag{4.5-38}
\end{gather*}
$$

For large values of $\phi$

$$
\begin{equation*}
\frac{2 \phi}{\sinh (2 \phi)} \rightarrow 0 \tag{4.5-39}
\end{equation*}
$$

The equation for $\lambda_{\text {opt }}$ then simplifies to

$$
\begin{equation*}
\lambda_{0}\left[\eta\left(1-5 \lambda_{0}\right)-\left(\lambda_{0} \eta-\frac{C_{3}}{C_{1}}\right)\right]=\left(\lambda_{0} \eta-\frac{C_{3}}{C_{1}}\right)\left(\frac{3-7 \lambda_{o}}{2}\right) \tag{4.5-40}
\end{equation*}
$$

For the chosen values of rate constant and diffusivity in the HDS system it was found that the assumption given by equation (4.5-39) is not valid. Hence equation (4,5-38) should be solved to determine the optimum pore radius, The limiting activity $C_{3}$ depends on the optimum initial activity (equation (4.5-23)), Hence equation (4.5-20) has to be solved for $\lambda_{i}$ before equation $(4,5-28)$ can be solved.

### 4.6 Parametric Study of Catalyst Performance

## 4.6-1 The Optimum Pore Radius

All the variables in equation $(4,5-38)$ viz $\phi, \eta, C_{3} / C_{1}$ can be expressed in terms of $\lambda_{0}$, the dimensionless group $\bar{\phi}$ and the fraction $F$ (equation (4,5-23)), For a given criterion of limiting activity (given choice of $F$ ) the optimum relative pore size $\lambda_{\text {opt }}$ depends only on the single dimensionless group $\tilde{\phi}$

$$
\begin{equation*}
\lambda_{\mathrm{opt}}=F(\tilde{\phi} \text { only }) \tag{4,6-1}
\end{equation*}
$$

This is a very significant and useful result,
The optimum pore radius variation with $\tilde{\phi}$ for different choices of limiting activity is shown in Fig. 4,11. The chosen value of F is indicated over each of the curves. The optimum pore radius increases with increase in $\tilde{\phi}$. This can be explained as follows.


FIG 4.II THE OPTIMUM PORE RADIUS FROM
THE ANALYTICAL EXPRESSION

Referring back to Fig. 4.4, initially the catalyst with the smaller sized pores and the larger surface area has the higher activity. This suggests that the reaction rate is controlled by the kinetics, After plugging catalysts with larger pores and a smaller surface area but a smaller resistance to diffusion have a higher activity, Hence at this stage the reaction rate is controlled by diffusion. The transfer from kinetic control to diffusion control causes the intersections in the graph - Fig. 4.4. The initial Thiele Modulus of the catalyst will determine when this transition to diffusion control will occur. If the initial Thiele Modulus is extremely small the reaction rate will be kinetic controlled for a long time and significant plugging is required to make diffusion effects important. On the other hand if the initial Thiele Modulus is high the reaction rate will swiftly become diffusion controlled.

When the initial Thiele Modulus is low and the reaction rate stays kinetic controlled for a long time, catalysts with smaller pores will have a higher activity over catalysts with larger pores for a longer period of time, Hence any change that lowers the Thiele Modulus will lower the optimal pore size. Changes that increase the Thiele Modulus will increase the optimal pore size.

In Fig, 4.11 it is seen that for any given $\widetilde{\phi}$ we have a larger optimum pore radius for lower choices of the limiting activity, Reduction in limiting activity implies that the catalyst is used for a longer time and is subjected to greater amount of plugging before being replaced. It was
seen in Fig. 4.2 that the optimum pore radius shifts to larger values due to plugging. Hence if the catalyst is going to be used till very low activity values, a larger pore radius will have an optimum overall activity. This explains the increase in optimal pore radius for a lower choice of limiting activity.

The optimum pore radius of the HDS system, for any choice of F can be directly obtained from Fig. 4.11 just with the knowledge of one dimensionless group $\tilde{\phi}$. However Fig, 4.11 is based on the solution of equation (4.5-38) which was obtained assuming a linear deactivation, Such an approach helped to establish the dependence of optimum relative pore size on a single dinensionless group. More accurate results on optimum pore radius can be obtained from the numerical solution of the effects of plugging. For a given value of the dimensionless group $\tilde{\phi}$ the methods of Chapter 3 were employed to generate the actual activity time curve (which departs from a linear behavior) for catalysts of different pore radii, Numerical integration was carried out to determine the area under the activity time curve. The optimal pore radius is then determined. These results of optimal pore radius are presented in Fig, 4.12,

It was found that the results in Figs. 4.11 and 4.12 are in close agreement showing linear deactivation is a good assumption to determine the optimum pore radius. At high values of Thiele Modulus the approximate method (using equation (4.5-38)) overestimates the optimum pore radius.


FIG 4.12 THE OPTIMUM PORE RADIUS FROM NUMERICAL METHOD

## 4.6-2 The Deactivation Rate

We have seen in Section 4.5 that the rate of deactivation can be approximately represented as

$$
\begin{equation*}
-\frac{\mathrm{dR}_{\ell}}{d t}=\frac{C_{1} \lambda_{o}^{2} \eta}{C_{2}\left(1-\lambda_{0}\right)} \tag{4.5-27}
\end{equation*}
$$

using equations (4.5-8) and (4,5-26)

$$
\begin{equation*}
-\frac{\mathrm{dR}_{\ell}}{\mathrm{dt}}=\frac{2 \alpha \mathrm{Mk}_{\mathrm{s}}^{2} \mathrm{C}_{\mathrm{A}_{\mathrm{b}}^{2}}^{2} \varepsilon \mathrm{~A}_{\ell} \mathrm{L}_{\ell} \eta}{\rho_{\mathrm{m}} \mathrm{a}_{\mathrm{o}}\left(\mathrm{a}_{\mathrm{o}}-\sigma\right)} \tag{4.6-2}
\end{equation*}
$$

This equation suggests a strong dependence for the rate of deactivar tion on the rate constant and bulk concentration and a weak dependence on diffusivity (since the diffusivity affects the effectiveness factor $\eta$ ). The deactivation rate is independent of molecular radius for small values of molecular radius (use $\sigma \ll a_{o}$ in equation (4.6-2)). When the molecular radius becomes comparable to pore radius, the catalyst effectiveness $\eta$ is considerably reduced. Hence the initial activity and the rate of deactivation, both of which are proportional to $\eta$ (equations (4.5-4) $\mathcal{G}$ (4.6-2)) are both reduced. Numerical calculations using methods of Chapter 3, verified these conclusions on the rate of deactivation. Increase in rate constant and bulk concentration and decrease in pore radius cause rapid deactivation even if they increase the activity temporarily. However increase in diffusivity and decrease in molecular size result in an increased activity without significant increase in the deactivation rate. It can be concluded that a higher diffusivity and a lower molecular radius always result in a better catalyst performance while a higher temperature need not necessarily mean a better performance.

When a catalyst loses a high percentage of its activity due to plugging the practice in industry is to increase the temperature. The increase of temperature while bolstering up the activity ( $\alpha \mathrm{k}^{\mathrm{n}}, 0.5 \leq n \leq 1$ ) temporarily, also increases the deactivation rate ( $\alpha \mathrm{k}^{2} \eta$ ) and is not necessarily the best cure. It can also be concluded that an optimization of temperature can be done in the same way as the optimization of pore size.

## CHAPTER 5

## IN $\operatorname{LUUENCE}$ OF CATALYST SHAPE ON ITS PERFORMANCE

### 5.1 Introduction

In the previous chapter the influence of plugging on a slab shaped catalyst was studied. Commercial catalysts are however closer to spherical in shape. In this Chapter, the pore plugging problem in a spherical catalyst will be solved. Studying the plugging in a spherical particle and comparing it with a slab is intended to reveal the presence, if any, of shape effects on catzlyst performance and optimum pore size.

One of the earliest models of a spherical catalyst was given by Wheeler [24]. This model averages the length of the pores in a sphere and represents a sphere by a group of pores of the same length, Newson [11] used this model to study the plugging in HDS reactor, In section 2.2 we saw that averaging of length alters the prevailing accessibility of pore structure. A representation of the catalyst particle that doesn't alter the accessibility and simulates the pore structure in the sphere is needed. Rester et al, [25] have proposed such a model.

## 5,2 Parallel Pore Model and Its Extension to Simulate Spherical Catalyst

## Plugging

This model proposed by Rester et al, represents the spherical catalyst by a system of non-intersecting parallel pores of varying length, All the pores originate at the outer surface of the catalyst and end at
varying points inside the spherical pellet.
Let $f(x) d x$ denote the fraction of the pore surface area lying at a depth between $x$ and $x+d x$ from the external surface of the particle. If there is uniform distribution of pore area at every point in the catalyst, we will have the same specific surface area (surface area per unit volume) everywhere in the catalyst, In that case the fraction of pore area at a depth between $x$ and $x+d x$ is the ratio of the elemental volume at that depth to the toral volume of the sphere,

For a sphere of radius $r$

$$
\begin{align*}
f(x) d x & =\frac{4 \pi(r-x)^{2} d x}{\frac{4}{3} \pi r^{3}}  \tag{5,2-1}\\
f(x) & =\frac{3}{r}\left(1-\frac{x}{r}\right)^{2} \tag{5.2-2}
\end{align*}
$$

Consider now a distribution of pores of initial radius $a_{o}$ for which $n(z) d z$ is the number of pores of length between $z$ and $z+d z$. At a distance x from the outer surface we have only those pores whose length is greater than or equal to $x$. The total pore surface area at a depth between $x$ and $x+d x$ is

$$
2 \pi a_{o} d x \int_{x}^{\infty} n(z) d z
$$

The total pore surface area in the catalyst is

$$
2 \pi a_{0} \int_{0}^{\infty} \ln (z) d z
$$

so that the function $f(x)$ defined above is

$$
\begin{equation*}
f(x)=\frac{\int_{x}^{\infty} n(z) d z}{\int_{0}^{\infty} \operatorname{zn}(z) d z} \tag{5.2-3}
\end{equation*}
$$

Since $f(x)=0$ for $x>r, n(z)=0$ for $z>r$ and we can replace the upper limits in these integrals by $r$. By differentiating with respect to $x$ we see that

$$
\begin{equation*}
-f^{\prime}(x)=\frac{n(x)}{\int_{0}^{r} \operatorname{zn}(z) d z} \tag{5,2-4}
\end{equation*}
$$

To apply this model we need to know the distribution function $n(z)$. From equations (5,2-2) and (5.2-4)

$$
\begin{equation*}
\frac{n(x)}{\int_{0}^{r} z n(z) d z}=\frac{6}{r^{2}}\left(1-\frac{x}{r}\right) \tag{5.2-5}
\end{equation*}
$$

The form of $n(x)$ that satisfies the above condition is

$$
\begin{equation*}
n(x)=k_{1}\left(1-\frac{x}{r}\right) \tag{5,2-6}
\end{equation*}
$$

where $k_{1}$ is an arbitrary constant.
The constant $k_{1}$ can be determined by equating the pore volume determined from the number distribution $n(z)$ to that obtained from the porosity. If $n(x) d x$ denotes the number of pores of length between $x$ and $x+d x$ in a spherical particle of radius $r$ and pore size $a_{o}$, it is evaident that

$$
\begin{equation*}
\pi a_{0}^{2} \int_{0}^{r} x n(x) d x=4 / 3 \pi r^{3} \varepsilon \tag{5,2-7}
\end{equation*}
$$

$$
\begin{equation*}
\pi a_{o}^{2} k_{1} \int_{0}^{r} x\left(1-\frac{x}{r}\right) d x=\frac{4}{3} \pi r^{3} \varepsilon \tag{5.2-8}
\end{equation*}
$$

which leads to

$$
\begin{equation*}
k_{1}=\frac{8 \varepsilon x}{a_{0}^{2}} \tag{5.2-9}
\end{equation*}
$$

Hence

$$
\begin{equation*}
n(x)=\frac{3 \varepsilon r}{a_{o}^{2}}\left(1-\frac{x}{r}\right) \tag{5,2-10}
\end{equation*}
$$

Since the pores are parallel and nonintersecting they act as independent units. The total reaction rate $R_{s p}$ in the catalyst particle can be obtained by summing $R$ over all the individual pores.

$$
\begin{align*}
R_{s p} & =\int_{0}^{r} n(x) R d x  \tag{5.2-11}\\
R_{s p} & =\frac{3 \varepsilon r}{2} \int_{0}^{r} R\left(1-\frac{x}{r}\right) d x  \tag{5.2-12}\\
& =\frac{8 \varepsilon r^{2}}{a_{0}^{2}} \int_{0}^{1} R(1-\xi) d \xi \tag{5.2-13}
\end{align*}
$$

where

$$
\begin{equation*}
\xi=x / r \tag{5.2--4}
\end{equation*}
$$

It should be noted that both $R_{s p}$ and $R$ are functions of catalyst age, t. The rate $R$ in a single pore of length $x$ can be obtained from the methods of Chapter 3. Equation (5.2-13) is then used to determine the reaction rate in a spherical particle.

The reaction rate $R$ in a single pore cannot be expressed as an explicit function of the pore length. It can numerically be determined for any specific value of the dimensioniess pore iength $\xi$. The usefil
method of integration under these conditions is the Gaussian Legendre quadrature. In this method the numerical value of the integrand is determined at a limited number of points inside the range of integration. A Lagrangian interpolation polynomial based on these values is used to represent the integrand throughout the range of integration.

For example, to determine

$$
\begin{equation*}
I=\int_{0}^{1} f(x) d x \tag{5,2-15}
\end{equation*}
$$

Express $f(x)=\sum_{i=1}^{N} f\left(x_{i}\right) Q_{i}(x)$
$Q_{i}(x)$ is a polynomial in $x$. The integration can be carried out analytically to give

$$
\begin{equation*}
I=\sum_{i=1}^{N} f\left(x_{i}\right) w\left(x_{i}\right) \tag{5.2-20}
\end{equation*}
$$

where $w\left(x_{i}\right)=\int_{0}^{1} Q_{i}(x) d x$
Thus the integral can be expressed as the weighted sum of the integrand evaluated at $N$ points. It is known that if $x_{i} s$ are chosen to be the
roots of the appropriate Jacobi polynomial (the shifted Legendre polynomial for the zero to one range) the accuracy of the quadrature is considerably enhanced. In that case, the roots $x_{i}, i=1 \ldots N$ and the corresponding weights $w\left(x_{i}\right)$ can be calculated from standard subroutines JCOBI and DFOPR described in the Appendix. Integration by such a method is known as the Gaussian Legendre quadrature. The number of collocation points, or the number of points at which the integrand has to be evaluated in this method, will be much less than the number of points required when integration is done by Simpson's Rule or other numerical methods. It has been found that five collocation points are sufficient to perform the integration in equation (5.2-13) to determine the reaction rate up to four significant digits. An increase of the number of collocation points alters the result only beyond four significant digits. The Gaussian Legendre quadrature is useful in predicting the activity in a sphere from calculation of activity of five pores of differing lengths given by the following values.

$$
\begin{aligned}
& \ell_{1}=0.04691008 \mathrm{r} \\
& \ell_{2}=0.2307635 \mathrm{r} \\
& \ell_{3}=0.5 \mathrm{r} \\
& \ell_{4}=0.7692347 \mathrm{r} \\
& \ell_{5}=0.9530899 \mathrm{r}
\end{aligned}
$$

The above $\frac{l i}{r}$ values are the roots of the fifth order shifted Legendre polynomial.

### 5.3 Comparisons Between Slab Catalyst and Spherical Catalyst

To examine shape effects the activity of the slab catalyst is compared with that of the spherical catalyst of the same volume to surface area ratio $\left(V_{p} / s_{x}\right)$. The ratio $\left(\frac{V_{p}}{s_{X}}\right)$ for a slab is its thickness $L_{\ell}$ while for a sphere it is a third of its radius. Given the thickness of the slab $L_{\ell}$ the radius of the sphere $r$ should be chosen such that

$$
\begin{equation*}
\mathrm{r}=3 \mathrm{~L}_{\ell} \tag{5.3-1}
\end{equation*}
$$

In addition to this we also specify the surface area $S_{x}$ to be the same for both catalysts.

$$
\begin{equation*}
A_{\ell}=4 \pi r^{2} \tag{5.3-2}
\end{equation*}
$$

We also specify the porosity, tortuosity and pore size to be the same in both catalysts.

The pore volume will be the same in both catalysts because the pellet volume and the porosity are constrained to be the same.

The total pore surface area $S$ of a spherical catalyst of radius $r$ is given by

$$
\begin{equation*}
S=\int_{0}^{r} n(x) 2 \pi a_{0} x d x \tag{5,3-3}
\end{equation*}
$$

using equations (5.2-10) and (5.2-14)

$$
\begin{align*}
S & =\left(\frac{8 \varepsilon r^{2}}{a_{o}^{2}}\right) r \int_{0}^{1} \xi(1-\xi) d \xi\left(2 \pi a_{0}\right)  \tag{5.3-4}\\
S & =\left(\frac{4 \varepsilon r^{2}}{a_{0}^{2}}\right) 2 \pi a_{0} \frac{r}{3} \\
& =\left(\frac{4 \pi r^{3} \varepsilon}{3}\right) \frac{2}{a_{0}} \tag{5,3-5}
\end{align*}
$$

The total pore surface area of a slab of area $A_{\ell}$ and thickness $L_{\ell}$ is given by

$$
S=n 2 \pi a_{o} L_{\ell}{ }^{T} \ell
$$

Substituting for $n$ from equation (4.1-2) and using equation (5.3-2)

$$
S=\left(\frac{4 \pi r^{3} \varepsilon}{3}\right) \frac{2}{a_{o}}
$$

The pore area, hence, is the same for both catalyst shapes. A slab of thickness $L_{\ell}$ and area $A_{\ell}$ (as given by equation (5.3-2)) will be equivalent to a spherical catalyst of radius $r$ (as given by equation (5.3-1)) in all respects - external surface area, volume, pore surface area, pore volume and number of pores. The difference is only in shape.

A comparison of slab and sphere is shown in Fig. 5.1. Initially the slab has a higher activity because its pore surfaces are more accessible than the pore surfaces in a sphere. The difference in the activity between the slab and the sphere diminishes as the catalyst ages.

Plugging makes the interior of the catalyst inaccessible to the reactants. The reaction occurs only at a small fraction of the pellet volume close to the outer surface. For all catalyst shapes this fraction of the pellet volume can be approximated as a slab. Hence shape effects diminish with plugging.

The maximum life of the catalyst is the same for both shapes because it is determined by pore mouth plugging which is shape independent.

The variation of demetallation activity with time for spherical catalysts with different pore sizes are compared in Fig. 5.2. The activity


## FIG 51 COMPARISON OF SLAB AND

 SPHERICAL CATALYSTStime curves intersect as in Fig. 4.4. A limiting activity which is a quarter of the optimal initial activity is marked by a dotted line. The area under the activity time curve for different pore radii are compared in the insert of Fig. 5.2. This shows an optimum pore radius of $52 \dot{A}$. The optimum obtained for a corresponding slab catalyst with the same set of parameters was (Fig. 4.4) 46 $\dot{\mathrm{A}}$.

It was observed in Section 4.6-1 that an increase in Thiele Modulus increased the optimal pore radius. Increase of Thiele Modulus makes the pore surface less accessible for the reactants and larger pores are required for optimal activity. It is known that, for the same Thiele Modulus the effectiveness factor of a spherical catalyst is lower than that of a slab. This is because the pore surface area in a sphere is less accessible. Hence for the same Thiele Modulus the optimal pore radius for a sphere is greater than that of a slab. One may speculate that any change of shape that reduces the accessibility of pore surface area increases the optimal pore size.

It is apparent from Fig. 5.2 that the deactivation in a spherical catalyst is approximately linear. The Rester et al. parallel pore model represents a sphere as a combination of pores of variable length while in Chapter 4 the slab was represented as a combination of pores of constant length. Thus a spherical catalyst is just an appropriate linear combination of slab catalysts of different pore lengths. For different values of Thiele Modulus (different values of pore length) the deactivation in a slab was found to be linear (section 4.4). Hence we can expect linear deactivation for a spherical catalyst.


FIG 5.2 COMPARISON OF PORE SIZES INA SPHERICAL CATALYST.

### 5.4 Expression for Optimum Pore Radius

## 5.4-1 Optimization of Initial Activity

The initial activity for a spherical catalyst described by the parallel pore model can be written as

$$
\begin{equation*}
R_{s p}=k_{s} C_{A_{b}} s \bar{n} \tag{5.4-1}
\end{equation*}
$$

Rester et al. [25] determined the expression for the effectiveness factor $\bar{n}$.

A straight pore of length $z$ has an effectiveness factor

$$
n(z)=\frac{\tanh (\phi(z))}{\phi(z)}
$$

The Thiele Modulus $\phi(z)$ which depends on the pore length can be expressed as a product of a constant $\phi_{1}$ and the length $z$

$$
\begin{aligned}
& \phi(z)=\phi_{1} z \\
& \eta(z)=\frac{\tanh \left[\phi_{1} z\right]}{\phi_{1} z}
\end{aligned}
$$

The catalytic surface area for a pore is proportional to its length $z$, so that it contributes to the total reaction rate proportionally to $\mathrm{zn}(\mathrm{z})$. The function $n(z)$ has been defined in equation (5.2-6). Thus the mean effectiveness factor will be

$$
\bar{n}=\frac{\int_{0}^{r} n(z) \tanh \left[\phi_{1} z\right] d z}{\int_{0}^{r} \phi_{1}^{z} z n(z) d z}
$$

using equation (5.2-4)

$$
\bar{\eta}=-\frac{1}{\phi_{1}} \int_{0}^{r} f^{\prime}(z) \tanh \left[\phi_{1} z\right] d z
$$

From equation (5.2-2) we can get

$$
f^{\prime}(z)=-\frac{6}{r^{2}}\left(1-\frac{z}{r}\right)
$$

We then make the transformation

$$
\zeta=\frac{2 \mathrm{~s}_{\mathrm{x}}}{\mathrm{~V}_{\mathrm{p}}}
$$

and note that the Thiele Modulus $\phi$ in a sphere is given by

$$
\phi=\frac{\phi_{1} V_{p}}{s_{x}}
$$

The effectiveness factor then becomes

$$
\begin{equation*}
\bar{\eta}=\frac{2}{3 \phi} \int_{0}^{3}\left(1-\frac{1}{3} \zeta\right) \tanh (\phi \zeta) d \zeta \tag{5.4-2}
\end{equation*}
$$

Thus

$$
\begin{equation*}
\bar{\eta}=F(\phi \text { on } 1 y) \tag{5.4-3}
\end{equation*}
$$

where $\quad \phi=\frac{r}{3} \sqrt{\frac{2 k_{s}}{a_{0} D e_{0}}}$
using equation (5.3-7) in equation (5.4-1)

$$
\begin{align*}
& R_{s p}=2 k_{s} C_{A_{b}} \varepsilon 4 \pi r^{2} \frac{r}{3 \sigma} \lambda_{o} \bar{\eta}  \tag{5.4-4}\\
& R_{s p}=C_{1} \lambda_{o} \bar{\eta} \tag{5.4-5}
\end{align*}
$$

where

$$
\begin{equation*}
C_{1}=\frac{2 k_{s} C_{A_{b}} \varepsilon 4 \pi r^{3}}{3 \sigma} \tag{5.4-6}
\end{equation*}
$$

From equations (5.3-1) and (5.3-2) it is evident that the constant $C_{1}$ is the same as defined for a slab in equation (4,5-8). The difference in activity between the slab and sphere arises only because the effectiveness
factor $\bar{\eta}$ is a different function of Thiele Modulus for a sphere.
For optimum initial activity

$$
\begin{align*}
& \frac{d}{d \lambda_{0}}\left(\lambda_{0} \bar{\eta}\right)=0  \tag{5.4-7}\\
& \lambda_{0} \bar{\eta}^{\prime}+\eta=0
\end{align*}
$$

Dividing throughout by $\bar{\eta}$

$$
\begin{aligned}
& \frac{\mathrm{d} \ell n \bar{\eta}}{\mathrm{~d} \ln \phi} \cdot \frac{\mathrm{~d} \ell n \phi}{\mathrm{~d} \ell \ln \lambda_{o}}+1=0 \\
& \frac{\mathrm{~d} \ell n \bar{\eta}}{\mathrm{~d} \ln \phi}=\frac{\phi}{\bar{\eta}} \frac{\mathrm{d} \bar{\eta}}{\mathrm{~d} \phi}=\frac{\phi}{\bar{\eta}} \frac{\mathrm{d}}{\mathrm{~d} \phi}\left\{\frac{2}{3 \phi} \int_{0}^{3}\left(1-\frac{1}{3} \zeta\right) \tanh [\phi \zeta] d \zeta\right\}
\end{aligned}
$$

using Leibnitz Rule

$$
\frac{\mathrm{d} \ln \bar{\eta}}{\mathrm{~d} \ln \phi}=\frac{2 \phi}{3 \bar{\eta}} \int_{0}^{3}\left(1-\frac{1}{3} \zeta\right) \frac{\partial}{\partial \phi}\left(\frac{\tanh [\phi \zeta]}{\phi}\right) \mathrm{d} \zeta
$$

The Thiele Modulus $\phi$ may be expressed as

$$
\begin{equation*}
\phi=\tilde{\phi} \sqrt{\frac{\lambda_{0}}{f\left(\lambda_{0}\right)}} \tag{5.4-8}
\end{equation*}
$$

where

$$
\begin{align*}
& \tilde{\phi}=\frac{r}{3} \sqrt{\frac{2 k_{s}^{\tau} s}{\sigma D_{A} \varepsilon}}  \tag{5.4-9}\\
& \frac{d \ell n \phi}{d \ell n \lambda_{o}}=\frac{1}{2}-\frac{1}{2} \frac{\lambda_{o} f^{\prime}}{f}
\end{align*}
$$

using equation (4.5-15)

$$
\frac{d \ln \phi}{d \ln \lambda_{o}}=\frac{1+3 \lambda_{o}}{2\left(1-\lambda_{o}\right)}
$$

Hence for optimum initial activity

$$
\begin{equation*}
\left(\frac{1+3 \lambda_{0}}{2\left(1-\lambda_{0}\right)}\right)\left(\frac{2 \phi}{3 \bar{\eta}} \int_{0}^{3}\left(\frac{\zeta}{3}-1\right) \frac{\partial}{\partial \phi}\left[\frac{\tanh (\phi \zeta)}{\phi}\right] J \zeta\right)=1 \tag{5.4-10}
\end{equation*}
$$

where $\bar{n}$ is given by equation (5.4-2).
The relative pore size $\lambda_{i s}$ for optimum initial activity in the spherical catalyst satisfies equation (5.4-10).

It is evident from equations $(5.4-3 \& 8)$ that $\lambda_{i s}$ depends only on $\tilde{\phi}$.

$$
\lambda_{i s}=F(\tilde{\phi} \text { only })
$$

We obtained

$$
\begin{equation*}
\bar{\eta}=\frac{2}{3} \bar{\phi} \int_{0}^{3}\left(1-\frac{1}{3} \zeta\right) \tanh (\phi \zeta) \mathrm{d} \zeta \tag{5.4-2}
\end{equation*}
$$

We can expand the hyperbolic tangent function around $\zeta=3$ $\tanh (\phi \zeta)=\tanh (3 \phi)+(\zeta-3) \phi \operatorname{sech}^{2}(3 \phi)+(\zeta-3)^{2} \phi^{2} \operatorname{sech}^{2}(3 \phi) \tanh (3 \phi)+\ldots$.

As $\phi$ becomes large the first term of the expansion becomes unity. The other terms become very small since $\operatorname{sech}(3 \phi) \sim 2, e^{3 \phi}$. Hence $\tanh (\phi 0)$ approaches unity for all values of $\zeta$. For large values of $\phi$

$$
\begin{aligned}
& \bar{n}=\frac{2}{3 \phi} \int_{0}^{3}\left(1-\frac{1}{3} \zeta\right) d \zeta \\
&=1 / \phi \\
& \frac{d \ln \bar{\eta}}{\mathrm{~d} \ln \phi}=-1
\end{aligned}
$$

Hence equation (5.4-10) becomes

$$
\frac{1+3 \lambda_{0}}{2-2 \lambda_{0}}=1
$$

which leads to $\lambda_{\text {is }}=1 / 5$.

The same result was obtained for the slab. Hence at high values of THiele Modulus the optimum pore radius becomes shape independent.

## 5.4-2 Optimization of Overall Activity

Let $\bar{\eta}_{i}$ denote the effectiveness factor corresponding to the optimum initial pore radius obtained from $\lambda_{i s}$. The limiting activity for the spherical catalyst $C_{3 s}$ can be chosen as a fraction $F$ of the optimal initial activity

$$
\begin{equation*}
C_{3 s}=C_{1} \lambda_{i s} \bar{\eta}_{i} F \tag{5.4-12}
\end{equation*}
$$

A catalyst has to be replaced when its activity falls below $\mathrm{C}_{3 \mathrm{~s}}$. The area under the activity time curve up to the limiting activity $C_{3 s}$, represents the cumulative activity of the catalyst. The cumulative activity has to be compared for catalysts of different pore sizes to establish an overall optimum.

The maximum life of the catalyst is shape independent and is

$$
\begin{equation*}
t_{m \ell}=\frac{C_{2}}{\lambda_{0}}\left(1-\lambda_{0}\right) \tag{4.5-25}
\end{equation*}
$$

where $\quad C_{2}=\frac{\rho_{m}{ }^{\sigma}}{\alpha k_{s} C_{b}{ }^{M}}$
Hence the rate of deactivation in a spherical catalyst is

$$
\begin{equation*}
\frac{-d R_{s p} p}{d t}=\frac{C_{1} \lambda_{0} \bar{\eta}}{\frac{C_{2}}{\lambda_{0}}\left(1-\lambda_{0}\right)} \tag{5.4-13}
\end{equation*}
$$

With the same reasonjing used to obtain equation (4.5-30) the cumulative activity $\bar{A}$ of the spherical catalyst can be represented as

$$
\begin{equation*}
\bar{A} \propto \frac{\left(1-\lambda_{0}\right)\left(\lambda_{o} \bar{\eta}-\frac{C_{3 \tilde{s}}}{C_{1}}\right)^{2}}{\lambda_{0}^{2} \bar{\eta}} \tag{5,4-14}
\end{equation*}
$$

For optimum pore radius

$$
\begin{equation*}
\frac{d \bar{A}}{d \lambda_{0}}=0 \tag{5.4-15}
\end{equation*}
$$

The similarity between equation (5.4-14) and equation (4.5-30) can be recognized.

Hence differentiation of equation (5.4-14) leads to

$$
\begin{gather*}
\lambda_{o}\left\{2\left(1-\lambda_{o}\right) \bar{\eta}\left[1+\frac{d \ell n \bar{\eta}}{d \ell n \phi}\left(\frac{1}{2}-\frac{\lambda_{o} f^{\prime}}{2 f}\right)\right]-\left(\lambda_{o} \bar{\eta}-\frac{C_{3 s}}{C_{1}}\right)\right\} \\
=\left(1-\lambda_{o}\right)\left(\lambda_{o} \bar{n}-\frac{C^{\prime} 3 s}{C_{1}}\right)\left[2+\frac{d \ln \bar{\eta}}{d \ln \phi}\left(\frac{1}{2}-\frac{\lambda_{o} f^{\prime}}{2 f}\right)\right] \tag{5.4-16}
\end{gather*}
$$

where $\bar{n}$ is defined by equation (5.4-2);

$$
\begin{equation*}
\frac{\mathrm{d} \ln \bar{\eta}}{\mathrm{~d} \ln \phi}=\frac{2 \phi}{3 \bar{\eta}} \int_{0}^{3}\left(1-\frac{1}{3} \zeta\right) \frac{\partial}{\partial \phi}\left(\frac{\tanh (\phi \zeta)}{\phi}\right) \mathrm{d} \zeta \tag{5.4-17}
\end{equation*}
$$

and $f=\frac{D_{e}}{\left(\frac{D_{A} \varepsilon}{\tau_{s}}\right)}$ and typically $f=\left(1-\lambda_{o}\right)^{4}$
From equation (5.4-12)

$$
\begin{equation*}
\frac{C_{3 s}}{C_{1}}=\lambda_{i s} \bar{\eta}_{i} F \tag{5.4-18}
\end{equation*}
$$

The optimum relative pore size $\lambda_{\text {opt, }}$ satisfies equation (5.4-16). Use of equations (5.4-2, 9 \& 18) helps us to express equation (5.4-16) in terms of $\lambda_{0}, \tilde{\phi}$ and F only. Hence $\lambda_{\text {opt, }}$ depends on $\tilde{\phi}$ and $F$ only. For a given criterion of limiting activity (given choice of F)

$$
\begin{equation*}
\lambda_{\text {opt }, \mathrm{s}}=\mathrm{F}(\tilde{\phi} \text { on } 1 \mathrm{y}) \tag{5.4-19}
\end{equation*}
$$

### 5.5 Parametric Study of Catalyst Performance

## 5.5-1 The Optimum Pore Radius

The numerical method described in section 5.2 was used to calculate the activity-time characteristics of spherical catalysts of different pore radii. Numerical integration was done to compare the cumulative activity for different pore radii and determine an optimum pore radius. The procedure was repeated for different values of the dimensionless group $\tilde{\phi}$ (defined by (5.4-9) and F (defined by (5.4-12)). Results are presented in Fig. 5.3. As in the case of the slab catalyst increase in $\tilde{\phi}$ and decrease in $F$ resulted in higher values of the optimal pore radius.

## 5.5-2 The Deactivation Rate

We have seen in section 5.4 that the rate of deactivation in a spherical catalyst can be approximately represented as

$$
\begin{equation*}
-\frac{d R_{s p}}{d t}=\frac{C_{1} \lambda_{o}^{2} \bar{n}}{C_{2}\left(1-\lambda_{o}\right)} \tag{5.4-12}
\end{equation*}
$$



FIG 5.3 OPTIMUM PORE RADIUS FOR SPHERICAL CATALYSTS
using equations (5.4-16) and (4.5-26)

$$
\begin{equation*}
-\frac{d R_{s p}}{d t}=\frac{2 \alpha M k_{s}^{2} C_{A_{b}}^{2} \varepsilon\left(4 \pi r^{3}\right) \bar{\eta}}{3 \rho_{m_{o}^{a}}\left(a_{o}-\sigma\right)} \tag{5.5-1}
\end{equation*}
$$

As in the slab catalyst the rate of deactivation is strongly dependent on the rate constant and bulk concentration and is weakly influenced by diffusivity (which affects the effectiveness factor $\bar{\eta}$ ). When we compare slab and spherical catalysts of same external volume and porosity, equation (5.5-1) is the same as the equation (4.6-2) representing the deactivation rate in a slab, except that for a given set of parameters the effectiveness factor $\bar{\eta}$ for a sphere is smaller than that of a slab. Hence the rate of deactivation of a spherical catalyst is lower than that of a slab exposed to the same conditions. This fact was observed in Fig. 5.1.

### 6.1 Effect of Pore Size Distribution on Catalyst Activity

Consider a slab catalyst of thickness $L_{\ell}$ and tortuosity $\tau_{\ell}$. The initial reaction rate $R$ in a single pore of radius a in this catalyst can be expressed in terms of the effectiveness factor $\eta$.

$$
\begin{equation*}
R=k_{s} C_{b} 2 \pi a \tau_{\ell} L_{\ell} \eta \tag{6.1-1}
\end{equation*}
$$

Let $f(a)$ da denote the number fraction of the pores in the catalyst having a radius between a and $a+d a$. Let $N_{\text {Tot }}$ denote the total number of pores in the catalyst. The overall rate $R_{\ell}$ can be expressed as a sunmation of rates in individual pores.

$$
\begin{equation*}
\mathrm{R}_{\ell}=\mathrm{N}_{\mathrm{Tot}} \int_{\mathrm{a}_{\min }}^{a_{\max }} \mathrm{Rf}(\mathrm{a}) \mathrm{da} \tag{5.1-2}
\end{equation*}
$$

Here we assume that the pores are non-interacting. Using equation (6.1-1)

$$
\begin{equation*}
R_{\ell}=N_{\operatorname{Tot}} 2 \pi k_{s} C_{A_{b}}{ }_{\ell} L_{\ell} \int_{a_{\min }}^{a \max } \operatorname{anf}(a) d a \tag{6.1-3}
\end{equation*}
$$

Let $f_{v}(a) d a$ denote the fraction of the pore volume contributed by pores of radius between $a$ and $a+d a$. The pore volume distribution $f_{v}(a)$ is more easily measurable than the number distribution $f(a)$. We need to express the number density function $f(a)$ in terms of the volume density function $f_{v}(a)$. The volume of pores of radius between $a$ and $a+d a$ can be expressed in terms of the two density functions. For a slab catalyst

$$
\begin{equation*}
\pi a^{2} L_{\ell}{ }_{\ell} N_{T o t} f(a) d a=\varepsilon A_{\ell} L_{\ell} f_{v}(a) d a \tag{6.1-4}
\end{equation*}
$$

which gives

$$
\begin{equation*}
N_{T o t} f(a) d a=\frac{\varepsilon A_{\ell} f_{v}(a) d a}{\pi a^{2} \tau_{\ell}} \tag{6.1-5}
\end{equation*}
$$

Substituting in equation (6.1-3)

$$
\begin{equation*}
R_{\ell}=2 k_{s} C_{A_{b}} \varepsilon A_{\ell} L_{\ell} \int_{a_{\min }}^{a} \frac{\eta}{a} f_{v}(a) d a \tag{6.1-6}
\end{equation*}
$$

The above equation suggests that the activity of a catalyst with a non-uniform pore size distribution is influenced by its harmonic ncan <a>, defined as

$$
\begin{equation*}
\frac{1}{<a>}=\int_{a_{\min }}^{{ }^{\max }} \frac{f_{v}(a) d a}{a} \tag{6.1-7}
\end{equation*}
$$

The pore surface area of the catalyst $S$ can be obtained as

$$
\begin{equation*}
\mathrm{S}=\int_{\mathrm{a}_{\min }}^{\mathrm{a} \max } 2 \pi a \mathrm{~L}_{\ell} \tau_{\ell} \mathrm{N}_{\mathrm{Tot}} \mathrm{f}(\mathrm{a}) \mathrm{da} \tag{6.1-8}
\end{equation*}
$$

using equation (6.1-4) we get

$$
\begin{equation*}
\mathrm{S}=\varepsilon \mathrm{A}_{\ell} \mathrm{L}_{\ell} \int_{\mathrm{a}_{\min }}^{\mathrm{a}_{\max }} \frac{2 \mathrm{f}_{\mathrm{v}}(\mathrm{a}) \mathrm{da}}{\mathrm{a}} \tag{6.1-9}
\end{equation*}
$$

It is therefore evident that the harmonic mean of any pore size distribution is that uniform pore size which will have the same pore surface area as the distribution for a given total pore volume $\varepsilon A_{\ell} L_{\ell}$.

The effectiveness factor $\eta$ can be represented as a Taylor's series around its value $\langle\eta\rangle$ at $a=\langle a\rangle$. Thus,

$$
\begin{equation*}
\eta=\langle\eta\rangle+\frac{d \eta}{d a}(a-\langle a\rangle)+\frac{1}{2} \frac{d^{2} \eta}{d a^{2}}(a-\langle a\rangle)^{2}+\ldots \tag{6.1-10}
\end{equation*}
$$

with the derivatives evaluated at $a=\langle a\rangle$.
As a first approximation the effectiveness factor can be represented by the first two terms in equation (6.1-10). Using this approximation in equation (6.1-6)

$$
\begin{align*}
R_{\ell} & \simeq 2 k_{s} C_{A_{b}} \varepsilon A_{\ell} L_{\ell}\left[\frac{\langle\eta\rangle}{\langle a\rangle}+\frac{d \eta}{d a}\left\{\int_{a_{\min }}^{a} \max f_{v}(a) d a-\langle a\rangle \int_{a_{\min }}^{a_{\max }} \frac{f_{v}(a) d a}{a}\right\}\right] \\
& =2 k_{s} C_{A_{b}} \varepsilon A_{\ell} L_{\ell} \frac{\langle\eta\rangle}{<a\rangle} \tag{6,1-11}
\end{align*}
$$

As a first approximation a catalyst with an arbitrary pore size distribution can be represented by its harmonic mean. A better approximation can be obtained by using the first threc terms in equation (6.1-10)

$$
\begin{align*}
& R_{\ell}=2 k_{s} C_{A_{b}} \varepsilon A_{\ell} L_{\ell}\left[\frac{\langle\eta\rangle}{\langle a\rangle}+\frac{1}{2} \frac{d^{2} \eta}{d a^{2}}\left\{\int_{a_{\min }}^{a \max } a f_{v}(a) d a+\langle a\rangle^{2} \int_{a_{\min }}^{a \max } \frac{f_{v}(a) d a}{a}\right.\right. \\
& \left.-2<a>^{2} \int_{a_{\min }}^{a_{\max }} \frac{f_{v}(a) d a}{a}-2<a>\int_{a_{\min }}^{a} f_{v}(a) d a\right\} \\
& =2 \mathrm{k}_{\mathrm{s}} \mathrm{C}_{\mathrm{A}_{b}} \varepsilon \mathrm{~A}_{\ell} \mathrm{L}_{\ell}\left[\frac{\langle\eta\rangle}{\langle\mathrm{a}\rangle}+\frac{1}{2} \frac{d^{2} \eta}{\mathrm{da}^{2}}(\overline{\mathrm{a}}-\langle\mathrm{a}\rangle)\right] \tag{6.1-12}
\end{align*}
$$

where $\overline{\mathrm{a}}$ is the arithmetic mean defined as

$$
\begin{equation*}
\bar{a}=\int_{a_{\min }}^{a} a f_{v}(a) d a \tag{6.1-13}
\end{equation*}
$$

An inequality established by Hardy [27] states that given a nonnegative weight function $f(a)$ and a function $\phi(a)$ such that $\phi^{\prime \prime}(a)$ is positive and finite for $0 \leq a \leq \infty$, then

$$
\frac{\int_{0}^{\infty} f(a) \phi(a) d a}{\int_{0}^{\infty} f(a) d a} \geq \phi\left[\frac{\int_{0}^{\infty} f(a) a d a}{\left[\int_{0}^{\infty} f(a) d a\right.}\right]
$$

We can choose $f(a)$ as the probability density function $f_{v}(a)$ and $\phi(a)=1 / 2$

Hardy's inequality becomes

$$
\begin{align*}
& \int_{0}^{\infty} \frac{f_{v}(a) d a}{a} \geq \phi[\bar{a}]=\frac{1}{\bar{a}} \\
& \int_{0}^{\infty} \frac{f_{v}(a) d a}{a} \geq \frac{1}{\bar{a}} \tag{6.1-14}
\end{align*}
$$

The equality is valid only when $f_{v}(a)=\delta(a-\bar{a})$. For non-uniform distributions the inequality of the above equation is valid. Hence for a non-uniform distribution using equation (6.1-7)

$$
\begin{align*}
& \langle a\rangle<\bar{a}  \tag{6.1-15}\\
& \frac{d^{2} \eta}{d a^{2}}=\frac{\eta}{a^{2}} \frac{d}{d \ell n a}\left(\frac{d \ell n \eta}{d \ln a}\right)=\frac{\eta}{a^{2}} \frac{d}{d \ell n \phi}\left(\frac{d \ell n \eta}{d \ell n \phi}\right)\left(\frac{d \ln \phi}{d \ln \lambda} \cdot \frac{d \ln \lambda}{d \ell n a}\right)^{2} \tag{6.1-16}
\end{align*}
$$

By definition, $\lambda=\sigma / a$

$$
\begin{equation*}
\frac{\mathrm{d} \ln \lambda}{\mathrm{~d} \ln a}=-1 \tag{6.1-17}
\end{equation*}
$$

Using equations (4.5-13, 15 ¢ 18)

$$
\begin{align*}
\frac{d^{2} \eta}{d a^{2}} & =-\frac{\eta}{a^{2}} \frac{d}{d \ln \phi}\left(\frac{2 \phi}{\sinh 2 \phi}-1\right)\left(\frac{1+3 \lambda}{2-2 \lambda}\right)^{2} \\
& =\frac{\eta}{a^{2}}\left(\frac{2 \phi(\tanh 2 \phi-2)}{\sinh (2 \phi) \tanh (2 \phi)}\right)\left(\frac{1+3 \lambda}{2-2 \lambda}\right)^{2} \tag{6.1-19}
\end{align*}
$$

$$
\tanh 2 \phi \leq 1 \quad \text { for } \quad 0 \leq \phi \leq \infty
$$

Hence

$$
\begin{equation*}
\frac{d^{2} \eta}{d a^{2}}<0 . \quad \text { for } \quad 0 \leq \phi \leq \infty \tag{6.1-20}
\end{equation*}
$$

It is evident from (6.1-15) and (6.1-20) that the correction term in equation (6.1-12) is negative. This shows that the activity in a catalyst with a non-uniform distribution will be less than that of a catalyst with a uniform pore radius equal to the harmonic mean of the distribution. The difference between the arithmetic and the harmonic means ( $\bar{a}-<a>$ ) depends on the variance of the distribution. Calculations on Gamma, Maxwell and other probability density functions showed that if the variance of the distribution is increased keeping the harmonic mean <a> constant, the difference ( $\overline{\mathrm{a}}-\langle\mathrm{a}>$ ) increases. Hence, according to (6.1-12) the activity $R_{\ell}$ should decrease with increase in variance.

Non-uniform pore size distributions can be represented to a first approximation by their harmonic mean. A desirable pore size distribution should therefore have its harmonic mean $\langle a\rangle=a_{\text {opt }}$, where $a_{o p t}$ is the optimum pore radius determined from Fig, 4.12. For a sharp distribution with a small variance ( $\bar{a}-\langle a\rangle$ ) will be small. Optimal activity can be obtained with a uniform distribution $f_{v}(a)=\delta\left(a-a_{\text {opt }}\right)$. A sharp
distribution with harmonic mean $\langle a\rangle=a_{\text {opt }}$ will have an activity close to this optimum and is the most desirable non-uniform distribution.

Numerical calculations were done on the effect of plugging in catalysts of different pore size distributions. They helped to verify the Taylor's series approximation used in this section and understand the effect of distribution on catalyst deactivation.

### 6.2 Numerical Method to Follow Deactivation of a Catalyst with Arbitrary

## Pore Size Distribution

The activity of the catalyst decreases with plugging. Equation (6.1-2) can be written as

$$
\begin{equation*}
R_{\ell}(t)=N_{T o t} \int_{a_{\min }}^{a} R(a, t) f(a) d a \tag{6.2-1}
\end{equation*}
$$

using equation (6.1-4)

$$
\begin{equation*}
R_{\ell}(t)=\frac{\varepsilon A_{\ell}}{\tau \ell} \int_{a_{\min }}^{a_{\max }} \frac{R(a, t) f_{v}(a) d a}{\pi a^{2}} \tag{6.2-2}
\end{equation*}
$$

The rate in a single pore $R(a, t)$ can be obtained from the numerical methods of Chapter 3. The above equation can be used to follow the deactivation in a slab catalyst. At any time $t, R(a, t)$ cannot be expressed as an explicit function of pore radius but can be computed numerically. The best method of performing the integration in equation (6.2.2) is by a Gaussian-Legendre quadrature. To use this method, the limits of integration should be zero and one.

Hence we define

$$
\begin{align*}
& a^{\prime}=\frac{a-a_{\min }}{a_{\max }-a_{\min }}  \tag{6.2-3}\\
& R_{\ell}(t)=\frac{\varepsilon A_{\ell}}{\tau_{\ell}}\left(a_{\max }{ }^{-a}{ }_{\min }\right) \int_{0}^{1 R\left(a^{\prime}, t\right) f_{v}\left(a^{\prime}\right) d a^{\prime}} \\
& \pi a^{2}
\end{align*}
$$

In this quadrature method, the integral is expressed as the weighted sum of the values of the integrand at a finite number of collocation points in the zero to one range. The collocation points and the weights can be determined from the subroutines JCOBI and DFOPR listed in the Appendix.

As the catalyst ages, the smallest pores become plugged to the point that free radius becomes equal to the molecular radius $(a=\sigma)$ and the reaction rate in them vanishes. Let $t_{\text {crit }}$ denote the time taken for the smallest of the pores (of radius $a_{\text {min }}$ ) to completely deactivate to zero reaction rate. Equation (3.2-16) which gives the rate of plugging can be integrated to give

$$
\begin{align*}
& a_{\min }-\sigma=\frac{a k_{s} C_{A_{b}}^{M}}{a_{\min ^{2}}{ }_{m}} t_{c r i t}  \tag{6.2-5}\\
& t_{\text {crit }}=\frac{a_{\min _{m}}\left(a_{m i n}-\sigma\right)}{\alpha k_{s} C_{b}^{M}} \tag{6,2-6}
\end{align*}
$$

For times larger than $t_{\text {crit }}$, pores larger than $a_{\text {min }}$ become completely deactivated. At any time $t$ greater then $t_{\text {crit }}$, we can find a pore radius. $a_{\text {crit }}$ such that reaction rate is zero for pores of radius below $a_{\text {crit }}$ and greater than zero for pores of radius greater than acrit. This means that pores that had an initial radius $a_{\text {crit }}$ are deactivated completely at
time t. Integration of equation (3.2-16) for pores of radius $a_{\text {crit }}$ gives

$$
\begin{equation*}
a_{\text {crit }^{-\sigma}}=\frac{a k_{s} C_{A_{b}}^{M}}{a_{c_{r i t}}{ }_{m}} t \tag{6.2-7}
\end{equation*}
$$

This equation defines $a_{\text {crit }}$ for any time $t$. The activity in a pore drops gradually till the pore mouth gets plugged and the free pore radius becomes equal to the molecular radius $(a=\sigma)$. Then the activity abruptly drops to zero (see Fig. 4.3). Hence for $t>t$ crit, $R(a, t)$ will be a discontinuous function of a as shown in Fig. 6.1 with a discontinuity at $a=a_{\text {crit }}$. When the Gaussian Legendre quadrature is used to integrate such a function, the results are uncertain even when a large number of (about 15) collocation points is used. This is because the Lagrangian interpolation doesn't fit the discontinuous function satisfactorily. To overcome this problem the integration in equation (6.2-2) must be carried out from the radius $a_{\text {crit }}^{+}$to $a_{\max }$ in which range the function $R(a, t)$ is continuous. For carrying out the Gaussian Legendre quadrature these new limits of integration are converted to a zero to one scale by defining

$$
\begin{equation*}
a^{\prime \prime}=\frac{a-a_{c r i t}}{{ }^{a} \max ^{-a} \text { crit }} \tag{6.2-8}
\end{equation*}
$$

To evaluate the integral, the integrand has to be evaluated at the roots of the shifted Legendre polynomial in the zero to one range. In other words, the integrand has to be evaluated for a fixed set of values of $a^{\prime \prime}$. However $a_{c r i t}$, the maximum radius for zero activity, is a function of time, increasing with time. It is apparent from equation (6.2-8) that the set of values of the pore radius a, at which the integrand must be


# FIg 61 DISCONTINUITY IN RATE FUNCTION 

evaluated changes with time. This makes it necessary to determine the reaction rate $R(a, t)$ for a new set of pore size values, every time the integration is carried out for a new catalyst age. To calculate reaction rate $R(a, t)$ in a pore of radius a at a time $t$ we have to simulate the plugging in the pore from time $t=0$. This will mean an enormous increase in computation effort. A more practical approach is to calculate $R(a, t)$ for a fixed set of values of a and use it in all integrations carried out for different catalyst ages. Let $R(a, t)$ be evaluated for $a_{i}, i=1 . . N$. For $t>t_{\text {crit }}$, the limits of integration are changed and $R(a, t)$ will be required for a different set of values of the pore radius, say $\bar{a}_{i}, i=1 \ldots N$. The set of values $R\left(\bar{a}_{i}, t\right)$ can be obtained from the known set of values $R\left(a_{i}, t\right)$ by Lagrangian interpolation. While using the Lagrangian interpolation we must make use of only those data points for which a is greater than $a_{\text {crit }}$, where $a_{\text {crit }}$ is obtained from equation (6.2-7). In that case the interpolation is done on that section of the function where it is continuous and hence reliable.

Thus the two essential precautions in the use of Gaussian Legendre quadrature are
(i) change of the lower limit of integration when the catalyst age exceeds a critical value as given by equation (6.2-6) so that $R(a, t)$ is always continuous throughout the range of integration.
(ii) Lagrangian interpolation should be used only on that section of the function $R(a, t)$ where it is continuous.

These precautions are essential because of the discontinuities in $R(a, t)$ for $t>t$ crit.

When these precautions were taken, it was found that nine collocation points were sufficient to attain a four digit accuracy on activity in the catalyst. This means, by calculating the activity for nine pore radii and weighing them appropriately we can predict activity in a catalyst having a continuous pore size distribution.

### 6.3 Adaptation of Standard Statistical Distributions to Represent Pore Volume Distribution

Gaussian, Gamma, Maxwell and Rayleigh were the four statistical distributions considered in this work to study the effect of pore size distribution on catalyst performance.

## 6.3-1 The Gamma Distribution

The Gamma probability density function is defined as

$$
\begin{equation*}
f(x)=\frac{1}{\Gamma(\alpha) \beta^{\alpha}} x^{\alpha-1} e^{-x / \beta} u(x) \tag{6.3-1}
\end{equation*}
$$

where $u(x)=1$ for $x>0$ and $u(x)=0$ for $x \leq 0 ; \alpha$ and $\beta$ are positive and $\Gamma(\alpha)$ is the well known Gamma function. For the above distribution

$$
\begin{equation*}
\text { mean } \mu=\beta \alpha \tag{6.3-2}
\end{equation*}
$$

the variance $\Sigma=\beta^{2} \alpha$
and the mode $=\beta(\alpha-1)$
For $\alpha=2, \beta=1$; we have $\mu=2, \sum=2$, mode $=1$ and

$$
\begin{equation*}
f(x)=x e^{-x} \tag{6.3-5}
\end{equation*}
$$

To use this probability density function to represent catalyst pore volume distribution with a mean of say $60 \dot{A}$, we make every unit of $x$
equivalent to $30 \dot{\mathrm{~A}}$. Then the distribution has a mode at $30 \dot{\mathrm{~A}}$ ( 1 unit). Variance $=2$ square units $=2 \times 30 \times 30=1800 \mathrm{sq} \dot{\mathrm{A}}$.

The Gamma distribution function extends up to infinity with very low probability at high values. In reality, catalyst pore size distribution has a finite upper cut off beyond which probability is zero. For statistical distributions which extend up to infinity the upper cut off can be chosen to be the point beyond which the probability is equal to one half of one percent. In other words,

$$
\begin{equation*}
F(x)=\int_{0}^{x} \max f(x) d x=0.995 \tag{6.3-6}
\end{equation*}
$$

will decide the choice of upper cut off.
For the function given by equation (6.3-5)

$$
F(x)=1-e^{-x}(1+x)
$$

It is found that $F(x)=0.997$ for $x=8$. Hence the upper cut off will be at $240 \dot{\mathrm{~A}}$ and the distribution has a span from $0 \dot{\mathrm{~A}}$ pore radius to $240 \dot{\mathrm{~A}}$.

We can alter the variance and the span of this distribution by changing the choice of $\alpha$ and $\beta$.

## 6.3-2 The Gaussian Distribution

The Gaussian probability density function is defined as

$$
\begin{equation*}
f(x)=\frac{1}{\sqrt{2 \pi \Sigma}} e^{-\frac{1}{2} \frac{(x-\mu)^{2}}{\Sigma}} \tag{6.3-7}
\end{equation*}
$$

The Gaussian distribution is symmetric and extends up to infinity on either side. The lower and upper cut off points can be chosen as

$$
\begin{align*}
& x_{\min }=\mu-2.5 \sqrt{\Sigma}  \tag{6.3-8}\\
& x_{\max }=\mu+2.5 \sqrt{\Sigma} \tag{6.3-9}
\end{align*}
$$

The probability in the range $x_{\min }$ to $x_{\max }$ will then be greater than $99.5 \%$. Calculations can be done for several values of the variance $\Sigma$ and the mean $\mu . \mu$ and $\Sigma$ have to be chosen so that $x_{\min } \geq 0$.

## 6.3-3 The Maxwell Distribution

The Maxwell probability density function is defined as

$$
\begin{equation*}
F(x)=\frac{\sqrt{2}}{a^{3} \sqrt{\pi}} x^{2} e^{-x^{2} / 2 \alpha^{2}} u(x) \tag{6.3-10}
\end{equation*}
$$

where $u(x)$ is the same as defined in section (6.3-1). The density function has the following properties

$$
\begin{align*}
& \mu=2 \alpha \sqrt{2 / \pi}  \tag{6.3-11}\\
& \Sigma=(3-8 / \pi) \alpha^{2} \tag{6.3-12}
\end{align*}
$$

For any given choice of $\alpha$ the unit of $x$ should be chosen such that $2 \alpha \sqrt{2 / \pi}$ units represent the selected mean. The variance depends on the choice of $\alpha$.

The Maxwell density function extends up to $+\infty$. To choose a finite upper cut off, the distribution function $F(x)$ has to be found.

$$
\begin{equation*}
F(x)=\int_{0}^{x} f(x) d x \tag{6,3-13}
\end{equation*}
$$

Carrying out the integration analytically we get

$$
\begin{equation*}
F(x)=\operatorname{erf}\left(\frac{x}{\sqrt{2 \alpha}}\right)-\frac{1}{\alpha} \sqrt{\frac{2}{\pi}} x e^{-x^{2} / 2 \alpha^{2}} \tag{6.3-14}
\end{equation*}
$$

For a given choice of $\alpha$ the value of $x$ for which $F(x)$ exceeds 0.995 can be chosen to represent the upper cut off.

## 6.3-4 Rayleigh Distribution

The Rayleigh density function is defined as

$$
\begin{equation*}
f(x)=\frac{x}{\alpha^{2}} e^{-x^{2} / 2 \alpha^{2}} \tag{6.3-15}
\end{equation*}
$$

with $\quad \mu=\alpha \sqrt{\pi / 2}$
and $\quad \Sigma=(2-\pi / 2) \alpha^{2}$
The distribution $F(x)$ defined in equation (6.3-13) can be obtained as

$$
\begin{equation*}
F(x)=1-e^{-x^{2} / 2 \alpha^{2}} \tag{6.3-16}
\end{equation*}
$$

The upper cut off in the distribution can be chosen as in the case of Maxwell distribution. Here again, change of $\alpha$ enables us to change the variance.

## 6.3-5 Bimodal Distribution

Many catalysts have a set of both micropores and macropores. This can be represented by a bimodal distribution. The micropore distribution and the macropore distribution do not normally interfere with each other since the order of pore sizes in macropores is much higher than that of the micropores. This fact simplifies the calculations on bimodal distributions. The activity of the catalyst can be calculated assuming only the micropore distribution were present. Another activity for the macropore distribution can also be computed. The sum of these two results gives the activity of the catalyst.

For example, consider a catalyst with a Gamma distribution of both micropores and macropores. The standard probability density function has to be multiplied by a suitable constant in both the distributions. The area under, say, the micropore distribution curve should not be unity, but equal to the fraction of the micropore volume to the total pore volume.

### 6.4 Results

The effect of variance for Gamma distribution is shown in Fig. 6.2. Activity variation with tine is shown for zero variance and variances of 200 and 400 Sq. A wi.th the same mean pore radius of $60 \dot{A}$. It is seen that the variance has a very small effect on catalyst performance. Change of variance from 0 to 200 square angstroms causes less than $4 \%$ difference in activity most of the time. An increase of the variance from 0 to 200 sq. $\dot{A}$ causes the catalyst to have a marginally higher initial activity and a faster rate of deactivation. We have seen that a decreased pore radius results in a higher initial activity (equation (4.5-6) ) and a faster rate of deactivation (equation (4.6-2)). Hence a catalyst with a mean pore radius of $60 \dot{A}$ and variance 200 sq. $\dot{A}$ behaves like a catalyst with uniform pores of radius less than $60 \dot{A}^{\circ}$. In this context, it is interesting to note that increase of variance from 0 to $200 \mathrm{sq} . \dot{\mathrm{A}}$ causes the harmonic mean to decrease from $60 \dot{\mathrm{~A}}$ to $57.3 \dot{A}$. This leads us to believe that the activity of a catalyst with a non-uniform pore size distribution is influenced by its harmonic mean.

Calculations on Gaussian, Maxwell and Rayleigh distributions lead to similar results. For all these distributions increase in variance means

a lower harmonic mean pore radius. Hence increase in variance caused the catalyst to have a marginally higher initial activity and a faster deactivation rate. In all the cases the effect of variance on catalyst performance was small. The weak dependence of the variance on the catalyst performance was earlier observed by Newson [11]. It may be due to the fact that increase in variance introduces both large and small pores and they compensate each other in their effects.

Fig. 6.3 compares catalysts with Maxwell distribution of differing variance and the same harmonic mean. The initial activity for all three cases are quite close. The small difference is due to the second derivative term of equation (6.1-13). The rate of deactivation is approximately the same in all three cases. This shows that as a good first approximation we can represent a catalyst by its harmonic mean pore radius. It is also seen from Fig. 6.3 that for the same harmonic mean increase in variance results in a poorer catalyst performance. Hence the most desirable nonuniform distribution is a narrow (low variance) distribution with a harmonic mean equal to the optimum pore radius determined from Fig. 4.12.

The Taylor's series approximation of revresenting a distribution by its harmonic mean is not always valid. One exception is the bimodal distribution. Equation (6.1-11) attempts to represent the effectiveness factor for all pore sizes in the distribution in terms of effectiveness at one pore size and derivatives at that point. Since the range of pore size is very wide in bimodal distribution this approximation isn't valid. However we can employ two Taylor's series expansions, one for the micropores and the other for macropores. This will mean representing a bimodal


FIG 6.3 EFFECT OF VARIANCE AT
CONSTANT HARMONIC MEAN


## FIG 6.4 APPROXIMATION FOR A BIMODAL GAMMA DISTRIBUTION

distribution by a distribution having only two pore sizes. (Two delta functions in the distribution). The two pore radii are the harmonic means of the micropore and macropore distribution. Fig. 6.4 shows that this representation is a good first approximation. From the same figure it is evident that the performance of the catalyst with a bimodal distribution is much poorer compared to that of a catalyst with uniform pore radius which is equal to the harmonic mean of the binodal distribution (45.1A). Same harmonic mean implies (equation (6.1-9)) same total pore surface area. Hence the same pore surface area is more effective when it is in pores of uniform radius than when it is spread out as a bimodal distribution of very small and very large pores. The bimodal distribution has a poorer performance because of its high variance.

It can be concluded that the ideal distribution is a uniform distribution with the pore radius equal to the optimum value determined from Figure 4.12. Any variance in the distribution causes reduction in activity. As the variance is increased the reduction is more.

## CHAPTER 7

## CONCLUSIONS

The importance of pore size distribution in hydrodesulfurization has already been recognized. In this work, numerical and analytical methods have been developed to follow deactivation by plugging for catalysts with arbitrary pore size distributions.

It was found that for a given total pore volume, the pore size distribution considerably affects the demetallation activity of the catalyst. Van Zoonen et al. [9] demonstrated that pelleting pressures can be altered to control the catalyst pore size distribution. Fience, the determination of an optimum pore size distribution can help improve the catalyst performance in a hydrodesulfurization reactor.

Spry and Sawyer [18] were the first to determine an optimum catalyst pore size for hydrodesulfurization. They optimised catalyst pore size based on its activity in the initial phase of the plugging. In the present work optimization was done based on the activity of the catalyst throughout its life span. It was shown that the actual optimum is greater than that determined by Spry and Sawyer. An expression for optimum pore radius was developed both for slab shaped and spherical catalysts. These show that the optimum relative pore size, which is the ratio of the optimum pore radius to the molecular radius depends only on a single dimensionless group $\tilde{\phi}$ given by

$$
\tilde{\phi}=\ell \sqrt{\frac{2 \mathrm{k}^{\tau}}{\mathrm{D}_{\mathrm{A}}{ }^{\varepsilon \sigma}}}
$$

The deactivation of the catalyst was found to be linear for a wide range of the Thiele Modulus. Expressions for rate of deactivation were developed for both slab shaped and spherical catalysts. In both cases the rate of deactivation is proportional to the square of the bulk concentration and is strongly influenced by the intrinsic rate constant $\left(\alpha k_{s}^{m} ; 1.5 \leq m \leq 2\right)$. For smaller sized reactant molecules ( $\sigma \ll a_{0}$ ) the deactivation rate is inversely proportional to the square of the pore radius. The rate of deactivation is only weakly influenced by reactant diffusivity $\left(\alpha \mathrm{D}_{\mathrm{e}}^{\mathrm{m}} ; 0 \leq \mathrm{m} \leq 0.5\right)$.

Comparisons of results of slab shaped and spherical catalysts showed that the shape of the catalyst influences the optimum pore radius. For the same Thiele Modulus, the optimum pore radius for a spherical catalyst is larger than that of a slab. It is conjectured that any change of shape that reduces the accessibility of pore surface increases the optimum pore radius.

The activity of a catalyst with an arbitrary pore size distribution can be represented as a first approximation by a catalyst of uniform pore size equal to the harmonic mean of the distribution. To get a better approximation we need to include a negative correction term that is related to the difference between the arithmatic mean and the harmonic mean of the distribution. Numerical calculations showed that for a given harmonic mean increase of variance of the distribution causes a reduction in demetallation capacity of the catalyst. Hence the ideal distribution is a uniform distribution. Since a uniform distribution is practically difficult to achieve, the most desirable pore size distribution is a distribution
of low variance with a harmonic mean equal to the optimum pore radius as determined from Fig. 4.12.

The major approximation in the present work is representing the reactant system by a single average molecular size. The asphaltenes in the residuum oil have quite a wide distribution of molecular radius. Future work can be focused on following the effects of plugging with a reactant systenı having an arbitrary molecular size distribution.

## NOMENCLATURE

## Unper Case

| A | $=$ | external surface area of the catalyst | $\mathrm{cm}^{2}$ |
| :---: | :---: | :---: | :---: |
| C | $=$ | concentration | gmoles $\mathrm{cm}^{-3}$ |
| D | = | diffusivity | $\mathrm{cm}^{2} \mathrm{sec}^{-1}$ |
| G | $=$ | local lag coefficient between macromolecule and wall |  |
| K | = | enhanced friction factor (ratio of pore to bulk friction coefficient for the macromolecule) |  |
| $\mathrm{K}_{1}$ | $=$ | constant, defined in equation (5.2-9) |  |
| L | $=$ | thickness of the catalyst | cm |
| M | = | molecular weight of the deposit material | gms gmole ${ }^{-1}$ |
| N | $=$ | axial mass flux (or) number of pores | gmoles $\mathrm{cm}^{-2} \mathrm{sec}^{-1}$ |
| T | $=$ | characteristic time of quasi steady state | sec |
| V | $=$ | velocity <br> (or) volume | $\mathrm{cmsec}_{\mathrm{cm}^{3}}^{-1}$ |

## Lower Case

| a | $=$ | pore radius | A |
| :---: | :---: | :---: | :---: |
| $\mathrm{c}_{1}$ | $=$ | constant defined in equation (4.5-8) | gmoles $\mathrm{sec}^{-1}$ |
| $c_{2}$ | $=$ | constant defined in equation (4.5-26) | sec |
| $\mathrm{c}_{3}$ | = | constant defined in equation (4.5-23) | gmoles $\mathrm{sec}^{-1}$ |
| $\mathrm{c}_{3 \mathrm{~s}}$ | = | constant defined in equation (5.4-12) | gmoles $\mathrm{sec}^{-1}$ |
| f | $=$ | $\mathrm{a} / \mathrm{a}_{0}=$ dimensionless pore radius |  |
| g | $=$ | De/De ${ }_{0}=$ dimensionless diffusivity |  |

$h \quad=\quad$ increment in dimensionless length
$\mathrm{k}=$ reaction rate constant
$\mathrm{cm} \sec ^{-1}$
$\ell=$ length of the pore cm
$\mathrm{m}=\operatorname{mass} \mathrm{gm}$
$r=$ radius of a spherical catalyst cm
s $=$ direction along metal deposit
$t=$ time sec
$x=$ distance from outer surface of the catalyst cm
$\mathrm{z}=\quad$ axial direction along a pore

Greek
$\alpha^{\prime}=$ stiochiometric factor
$\alpha=(1-\gamma) \alpha^{\prime}$
(or) parameter in Gamma, Maxwell and Rayleigh distributions
$\beta=$ dimensionless plug thickness $=\delta / a_{0}$ (or) parameter in Gamma distribution
$\gamma=$ ratio of slow cake deposition rate to metal sulphide deposition rate
$\delta \quad=\quad$ plug thickness
$\varepsilon \quad=\quad$ catalyst porosity
$\eta \quad=\quad$ dimensionless length $=z / \ell$
(or) effectiveness factor in a slab
$\bar{n} \quad=\quad$ average effectiveness factor in a spherical catalyst modelled as a system of parallel pores
$\tau=$ tortuosity of the catalyst
$\rho=$ density
$\mathrm{gms} \mathrm{cm}{ }^{-3}$

| $\sigma$ | $=$ | radius of the molecule | A |
| :---: | :---: | :---: | :---: |
| $\xi$ | $=$ | $\mathrm{x} / \mathrm{r}$ |  |
| $\lambda$ | $=$ | ratio of the molecular radius to free pore radius $=\sigma / a$ |  |
| $\psi$ | $=$ | dimensionless concentration $=c / c_{b}$ |  |
| $\phi$ | $=$ | $\text { Thiele Modulus }=2 \sqrt{\frac{2 k_{s}}{a_{0} D e_{0}}}$ |  |
| $\phi_{1}$ | $=$ | $\phi / \ell$ | $\mathrm{cm}^{-1}$ |
| $\tilde{\phi}$ | $=$ | $\tau_{\ell} L_{\ell} \sqrt{\frac{2 k_{s} \tau_{\ell}}{D_{A} \varepsilon \sigma}} \text { for slab }$ |  |
|  | $=$ | $R / 3 \sqrt{\frac{2 k_{s}{ }^{\tau} s}{D_{A} \varepsilon \sigma}} \quad$ for sphere |  |
| $\Sigma$ | $=$ | variance of the distribution | Sq A |
| $\mu$ | $=$ | mean pore radius of the distribution | $\dot{\text { A }}$ |

## Subscripts

```
    A = property of species A
    b = bu1k
crit = critical
    e = effective
    eq = equivalent
    i = based on initial activity
    \ell = pertaining to a slab catalyst
        (or) life of the catalyst
    m = property of deposit
```

```
max = maximum
    m\ell = maximum life
min = minimum
    o = initial
opt = optimum
    s = surface area based
    sp = pertaining to a spherical catalyst
Tot = total
```


## BIBLIOGRAPHY

1. Mckinney, J.D., Stipanovich, I. Hydrocarbon Process, 97 (1971)
2. Richardson, R.L., Alley, S.K. Preprints, Division of Petroleum Chemistry, American Chemical Society. 20, (2), 554-563 (1975)
3. Dickie, J.P., Yen, T.F. Preprints, Division of Petroleum Chemistry, American Chemical Society. 12, (2) B-117 (1967)
4. Dautzenberg, F.M., Van Klinken, J., Pronk, K.M.A., Sie, S.I., and Wijffels, J.B. Paper to be presented at the fifth International Symposium. Chemical Reaction Engineering, Houston, March 13-15,1978.
5. Beuther, H., Schmid, B. Sixth World Petroleum Congress, Frankfurt, West Germany, June 21,1963, Section 3, Paper 20, 297-307.
6. Moritz, K.H. et al. Fuel oil Desulfurisation Symposium, Japan Petroleum Institute, Tokyo, March 10-11, 1970.
7. Shah, Y.T., Paraskos. Industrial And Engineering Chemistry Process Design And Development. 14, 368 (1975)
8. Schuit, G.C.A., Gates, B.C. AICHE Journal 19, 417, (1973)
9. Van Zoonen, Douves, C.T. Journal of the Institute of Petroleum. 49, (480), 383, (1963)
10. Newson, E.J. Preprints, Division of Petroleum Chemistry, American Chemical Society. Al41-152 (1970)
11. Newson, E.J. Industrial And Engineering Chemistry Process Design And Development. 14, 27 (1975)
12. Hughes, C.C., Mann, R. To be published. American Chemical Society Symposium Series.
13. Larson, O.A., Beuther, H. Preprints, Division of Petroleum Chemistry, American Chemical Society. 11, B-95 (1966)
14. Scott, J.W. et al. Fuel oil desulfurisation Symposium, Japan Petroleum Institute. Tokyo, March 10-11, 1970.
15. Frye, C.G., Mosby, J.F. Chemical Engineering Progress. 63, 66 (1967)
16. Hoog, H. Journal of the Institute of Petroleum. 36, 738 (1950)
17. Oxenreiter, M.F. et al. Fuel oil desulfurisation Symposium. Japan Petroleum Institute. Tokyo, November 29, 1972.
18. Spry, J.C.Jr, Sawyer, W.H. Paper 30c, 68th AICHE Meeting, Los Angeles, (1975)
19. Henke, A.M. Fuel oil desulfurisation Symposium, Japan Petroleum Institute. Tokyo, March 10-11, 1970.
20. Pichler, H. et al. Petroleum Refiner. 36, (9), 201-204 (1957)
21. Ferry, J.L. Journal of General Physiology. 20, 95 (1936)
22. Giddings, J.C., Kucera, E., Russel, C.P. and Meyers, M.N. Jo!rnal of Physical Chemistry. 72, 4397 (1968)
23. Anderson, J.L., Quinn, J.A. Biophysical Journa1. 14, 130 (1974)
24. Wheeler, A. Advances in Catalysis. 3, 250 (1951)
25. Rester, S., Jouven, J., Aris, R. Chemical Engineering Science. 24,1019 (1969)
26. Rester, S., Aris, R. Chemical Engineering Science. 24, 793 (1969)
27. Hardy, G.H., Littlewood, J.E., Polya, G. Inequalities. Cambridge University Press. 150 (1934)

## APPENDIX

## A-1 Thomas Algorithm

This algorithm can be used to solve for the unknown column matrix $\overline{\mathrm{x}}$ of $n$ elements, in the relation

$$
\begin{equation*}
\overline{\overline{\mathrm{A}}} \overline{\mathrm{x}}=\overline{\mathrm{d}} \tag{A-1-1}
\end{equation*}
$$

where $\bar{d}$ is a known column matrix of $n$ elements and $\overline{\bar{A}}$ is a nxn tridiagonal matrix

$$
\overline{\bar{A}}=\left[\begin{array}{llllll}
a_{1} & b_{1} & & & & \\
c_{2} & a_{2} & b_{2} & & & \\
& c_{3} & a_{3} & b_{3} & & \\
& & & & & \\
& & & & & b_{n-1} \\
& & & & c_{n} & a_{n}
\end{array}\right]
$$

We define

$$
{ }^{w_{1}}=a_{1}
$$

$$
w_{r}=a_{r}-c_{r} q_{r-1}
$$

$$
r=2,3 \ldots n
$$

$$
q_{r-1}=\frac{b_{r-1}}{w_{r-1}}
$$

and $\quad g_{1}=\frac{\mathrm{d}_{1}}{\mathrm{w}_{1}}$

$$
g_{r}=\frac{d_{r}-c_{r} g_{r-1}}{w_{r}} \quad r=2,3 \ldots n
$$

The unknown matrix $\bar{x}$ can then be obtained as

$$
\begin{array}{ll}
x_{n}=g_{n} & (A-1-3) \\
x_{r}=g_{r}-q_{r} x_{r+1} & r=1,2 \ldots n-1
\end{array}
$$

```
    SUBROUTINE JCOBI(ND,N,NO,NI,AL,BE,FA,FB,FC,RCOT)
    IMPLICIT REAL*8(A-H,O-Z)
    CIMENSION FA(ND),FB(ND),FC(ND),ROOT(ND)
    AR=AL+BE
    AD=BE-AL
    AP=BE*AL
    FA(1)=(AD/(AB+2.)+1.)/2.
    FB(1)=0.
    CO 10 I=2,N
    Z1=DFLOAT(I)-1.
    Z=AB+2.*Z1
    FA(I)=(AB/Z*AD/(Z+2.)+1.)/2.
        IF(I-2) 11,12,11
    12 FB(I)=(AB+AP+Z1)/Z/Z/(Z+1.)
        GO TO 10
    11 Z=Z*Z
        Y=Z1*(AB+Z1)
        Y=Y*(AP+Y)
        FB(I)=Y/Z/(Z-1.)
    10 CONTINUE
        x=0.
        00 20 I= I,N
        I 1 = 1-1
25 x }0=0
```

$X N=1$ 。
$X D 1=0$ 。
$X_{N} 1=0$ 。
CO $30 \mathrm{~J}=1, \mathrm{~N}$
$X P=(F A(J)-X) \neq X N-F B(J) * X D$
$X P 1=(F A(J)-X) \neq X N 1-F B(J) * X D 1-X N$
$X D=X N$
$X D I=X N 1$
$X V=X P$
$30 \quad X N 1=X P 1$
$Z C=1$ 。
$Z=X N / X N 1$
IF(I1) 21,21,22
22 DO $23 \mathrm{~J}=1, \mathrm{I} 1$
$23 \quad Z C=Z C-Z /(X-\operatorname{RCOT}(J))$
$21 \quad Z=Z / Z C$
$x=x-Z$
IF ( CABS (Z)-1.E-7) 26,26,25
$26 \operatorname{ROOT}(I)=x$
$x=x+. \cos 5$
20 CONT INUE
$N T=N+N O+N L$
IF (NO-1) $35,36,35$
36 DO $42 \quad I=1, N$
$J=N+1-I$
51: ROOT(1)=0.
52:
53:
54:
55:
56:
57:
58:
59:
60:
61:
62:
63:
64:
65:
66:
67:

```
```

```
50: 42 ROOT(J+1)=ROOT(J)
```

```
50: 42 ROOT(J+1)=ROOT(J)
```

    35 IF(N1-1) 38,37,38
    ```
    35 IF(N1-1) 38,37,38
    37 ROOT(NT)=1.
    37 ROOT(NT)=1.
    38 CO 40 I=1,NT
    38 CO 40 I=1,NT
        y=ROOT(I)
        y=ROOT(I)
        FA(I)=1.
        FA(I)=1.
        FB(I)=0.
        FB(I)=0.
        FC(I)=0.
        FC(I)=0.
        DO 40 J=1,NT
        DO 40 J=1,NT
        IF (J-I) 41,40,41
        IF (J-I) 41,40,41
    41 Y=X-RCOT(J)
    41 Y=X-RCOT(J)
        FC(I)=FC(I)*Y+ 3**FB(I)
        FC(I)=FC(I)*Y+ 3**FB(I)
        FB(I)=Y*FE(I)+2.*FA(I)
        FB(I)=Y*FE(I)+2.*FA(I)
        FA(I)=Y*FA(I)
        FA(I)=Y*FA(I)
    40 CONTINUE
    40 CONTINUE
        RETURN
        RETURN
        ENE
```

        ENE
    ```
```

    SUBROUTINE DFOPRIND,N,NC,NI,I,IO,FA,FB,FC,RCOT,VECT)
    IMPLICIT REAL*8(A-H,O-Z)
    CIMENSION FA(ND),FB(ND),FC(ND),ROOT(NDI,VECT(ND)
    NT}=\textrm{N}+\textrm{NO}+\textrm{N}
    IF(IC-3) 1,10,10
    1 [O 20 J=1,NT
        IF (J-I) 21,2,21
    2 IF(ID-1) 5,4,5
    4 VECT(I)=FE(I)/FA(I)/2.
        GO TO 20
    5 VECT(I)=FC(I)/FA(I)/3.
        GO TO 20
    21 Y=ROOT(I)-ROCT(J)
        VECT(J)=FA(I)/FA(J)/Y
        IF (ID-2) 20,22,20
        VECT(J)=VECT(J)*(FB(I)/FA(I)-2./Y)
    20 continue
        GO TO 50
    10 Y=0.
        IF (IO-4) 31,30,31
    31 DO 25 J=1,NT
        X=ROOT(J)
        AX=X* (1,-X)
        IF (NO) 2t,27,26
    ```
\begin{tabular}{|c|c|c|}
\hline 25: & 27 & \(\Delta x=A x / X / X\) \\
\hline 26: & 26 & IF(N1) 28,29,28 \\
\hline 27: & 29 & \(\Delta X=A X /(1 .-X) /(1,-X)\) \\
\hline 28: & 28 & \(\operatorname{VECT}(J)=A X / F A(J) / F A(J)\) \\
\hline 29: & 25 & \(Y=Y+V E C T(J)\) \\
\hline 30: & & GO TO 60 \\
\hline 31: & 30 & CO \(35 \mathrm{~J}=1, \mathrm{NT}\) \\
\hline 32: & & \(x=R O T T(J)\) \\
\hline 33: & & IF (NO) \(36,37,36\) \\
\hline 34 : & 37 & \(\Delta \mathrm{X}=1 . / \mathrm{X}\) \\
\hline 35: & 36 & IF(N1) \(38,39,38\) \\
\hline 36: & 39 & \(A X=1 . /(1,-X)\) \\
\hline 37: & 38 & \(\operatorname{VECT}(J)=A X / F A(J) / F A(J)\) \\
\hline 38: & 35 & \(Y=Y+V E C T(J)\) \\
\hline 29: & 60 & DO \(61 \mathrm{~J}=1, \mathrm{NT}\) \\
\hline 40: & 61 & \(\operatorname{VECT}(J)=\operatorname{VECT}(J) / Y\) \\
\hline 41: & 50 & RETURN \\
\hline 42: & & END \\
\hline
\end{tabular}```

