

2/16/99

## Rate Data      Chapter 5

- 1) Given Concentration vs time data determine the reaction rate
- 2) Devise an experiment to determine a reaction rate.

Two techniques

$C$  vs  $t$

in batch reactors

$C$

in differential reactors

homogeneous reactions

6 methods to analyze data

solid fluid reactions

### Batch Reactor

Goal is to find  $r = f(C_i, C_j, \dots)$

determine expression

then evaluate constants

22-141 50 SHEETS  
22-142 100 SHEETS  
22-144 200 SHEETS



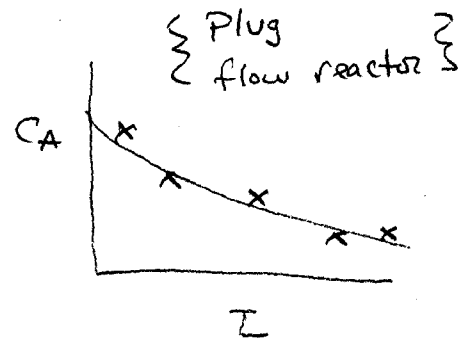
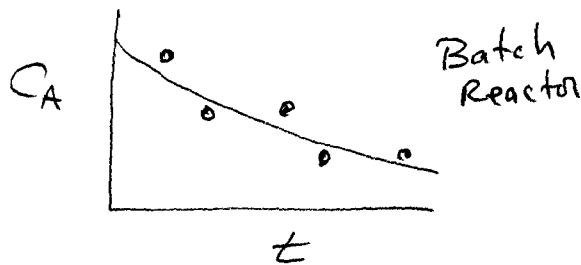
How do we get values of  $v_A$  vs  $C_A$  ?

$$\frac{d(C_A V)}{dt} = 0 - 0 + v_A V \quad \left. \vphantom{\frac{d(C_A V)}{dt}} \right\} \text{Batch Reactor}$$

$$\frac{dC_A}{dt} = \dot{v}_A = -R_{CA} \quad \text{B}$$

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln(-r_A) = \ln k + \alpha \ln C_A + \beta \ln C_B$$

What data do we collect ?



Procedure:

fit  $C_A$  vs  $t$  to  $C_A = A + Bt + Ct^2 \dots$   
or other equation

→ differentiate this expression

$$\frac{dC_A}{dt} = 0 + B + 2Ct + 3Dt^2 \dots$$

Now plot  $\frac{dC_A}{dt}$  vs  $C_A$

# Batch Reactors :

## 5.1.1 Differential method

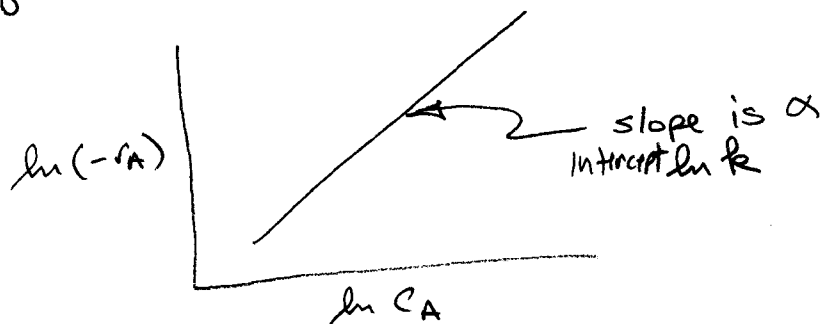
Assume reaction is irreversible

### I. $A \rightarrow \text{products}$

Assume:  $r_A = -k C_A^\alpha$  find  $k$  and  $\alpha$

$$\ln(-r_A) = \ln k + \alpha \ln C_A$$

make a plot of  $\ln(-r_A)$  vs.  $\ln C_A$



### II. $A + B \rightarrow \text{products}$

(and the reaction is assumed to be irreversible)

Assume:  $r_A = -k C_A^\alpha C_B^\beta$

USE method of excess with differential method

1)  $r_A = -\left(k C_{A_0}^\alpha\right) C_B^\beta$  excess in A

2)  $r_A = -\left(k C_{B_0}^\beta\right) C_A^\alpha$  excess in B

(More options later)

Example of Differential Rate Method

Data at T= 100 °C      3 order fit      4 order fit

Answer  
alpha= 0.8

t (min)	CA (mol/L)	CA (mol/L) Data fit	-dC/dt	CA (mol/L) Data fit	-dC/dt
0	20	19.95	2.13	19.999	2.1941
2	15.98	16.01	1.82	15.97706	1.835538
4	12.63	12.67	1.53	12.62714	1.521535
6	9.86	9.88	1.27	9.863414	1.248797
8	7.61	7.59	1.03	7.606642	1.014029
10	5.79	5.74	0.83	5.78418	0.813938
15	2.71	2.67	0.43	2.710836	0.4438
18	1.61	1.63	0.27	1.615093	0.294449
20	1.11	1.16	0.20	1.10508	0.218324
25	0.37	0.35	0.15	0.372281	0.086037

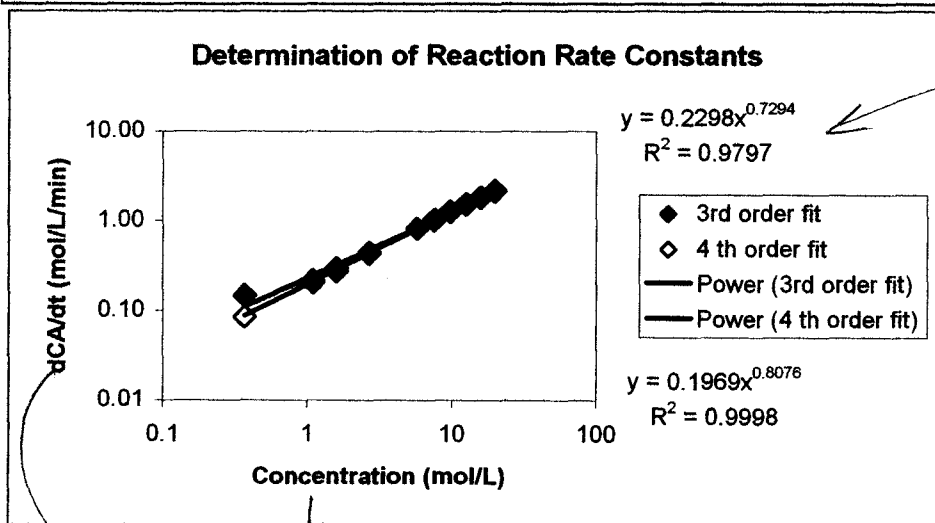
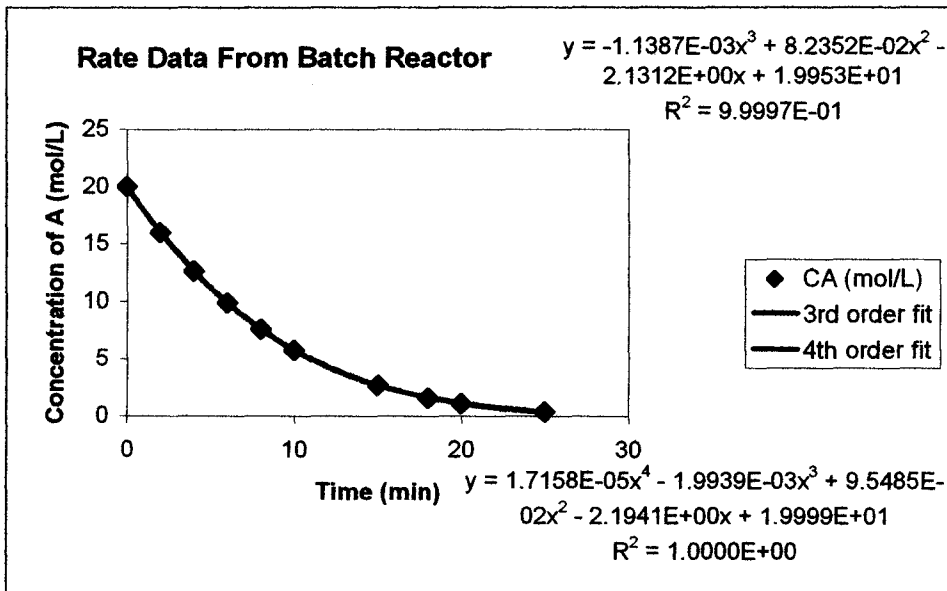
k= 0.2 min<sup>-1</sup>

4th order fits:

$$CA = 0.000017158 \cdot CA^{16^4} - 0.0019939 \cdot CA^{16^3} + 0.095485 \cdot CA^{16^2} - 2.1941 \cdot CA^{16} + 19.999$$

$$-dCA/dt = -(0.000017158 \cdot CA^{16^3 \cdot 4} - 0.0019939 \cdot CA^{16^2 \cdot 3} + 0.095485 \cdot CA^{16^1 \cdot 2} - 2.1941)$$

Leave out last data point for better fit

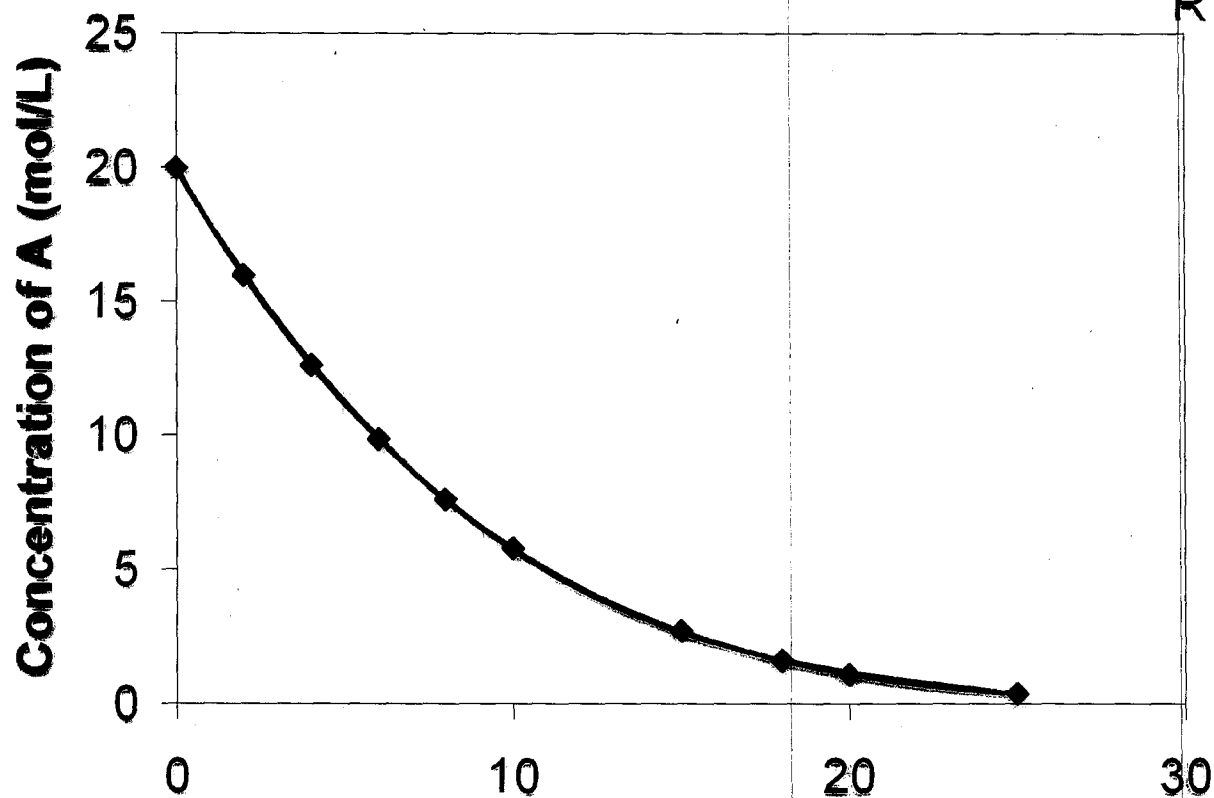


Notice Power law fit

ln-ln scale

# Rate Data From Batch Reactor

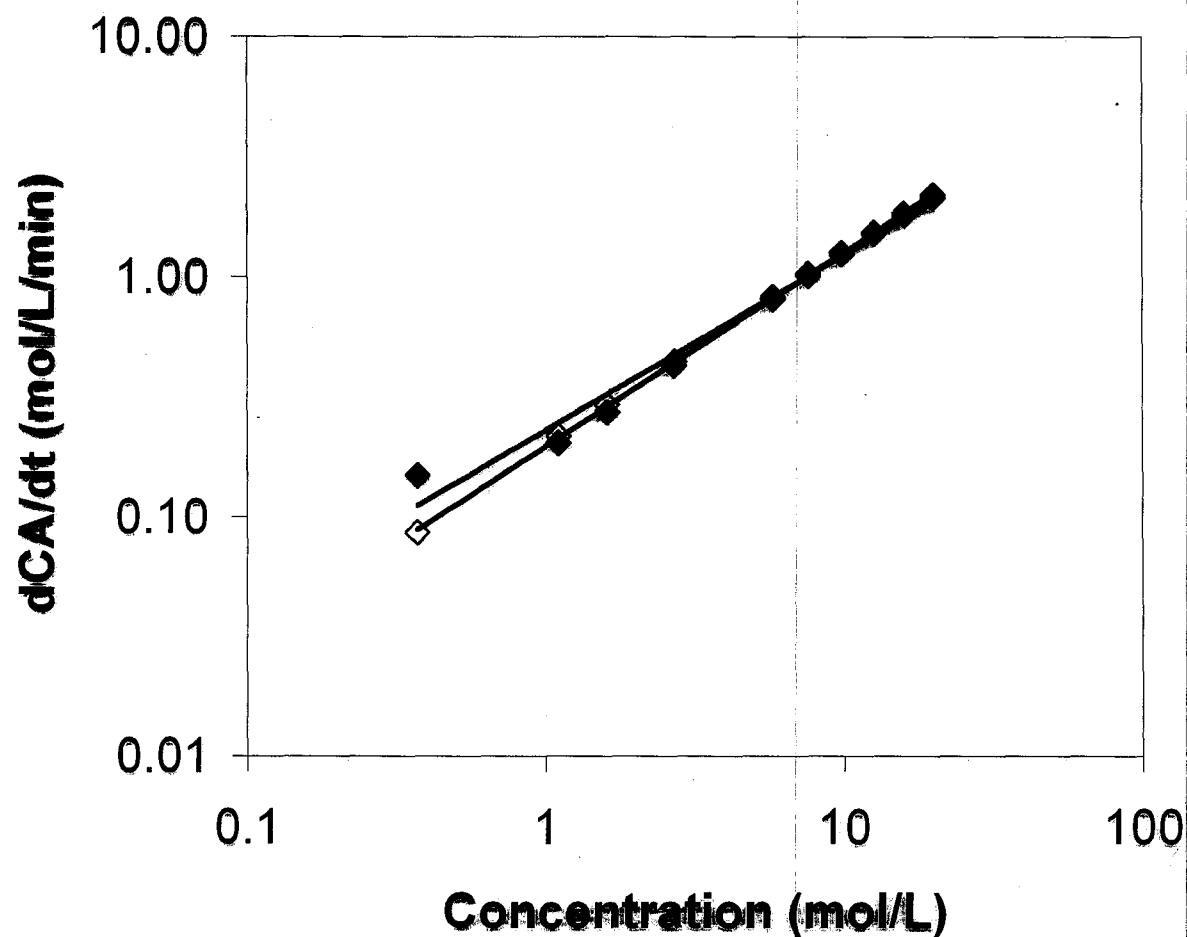
$$y = -1.1387E-03x^3 + 8.2352E-02x^2 - 2.1312E+00x + 1.9953E+01$$
$$R^2 = 9.9997E-01$$



- ◆ CA (mol/L)
- 3rd order fit
- 4th order fit

$$\text{Time (min)} = 1.7158E-05x^4 - 1.9939E-03x^3 + 9.5485E-02x^2 - 2.1941E+00x + 1.9999E+01$$
$$R^2 = 1.0000E+00$$

## Determination of Reaction Rate Constants: Differential Method



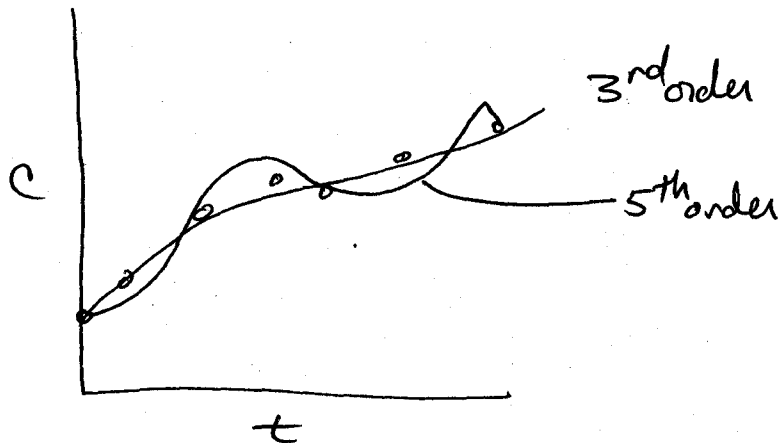
$$y = 0.2298x^{0.7294}$$
$$R^2 = 0.9797$$

- ◆ 3rd order fit
- ◇ 4th order fit
- Power (3rd order fit)
- Power (4th order fit)

$$y = 0.1969x^{0.8076}$$
$$R^2 = 0.9998$$

Be careful with polynomials

Figure 5-2 a ≠ b



$$C = a + bt + ct^2 + dt^3$$

Procedure

- 1) postulate rate law
- 2) Rewrite mole balance in terms of measured value  $C$  or  $P$
- 3) Look for simplifications in rate expression
- 4) Batch  $dC/dt$
- 5) determine  $k$
- e) Repeat for several  $T$  to find  $E_A$  and  $A$   
 $k = A \exp(-E_A/RT)$

NEXT METHOD  
Batch Reactor - Integral method (5.1.2)

Started 11/16/90 5-5

- Procedure
1. Guess Reaction rate law  $r = -k C_A^2 C_B^3 \therefore \alpha \neq \beta$  Numbers
  2. Integrate reactor mole balance
  3. Plot appropriate quantities of Conc. and time using experimental data.

mole Balance:  $\frac{dC_A}{dt} = -r_A$  with stoic.  $A + B \rightarrow C$

\* USE EXCESS OF B

$$\frac{dC_A}{dt} = \underbrace{(k C_{B_{0E}}^3)}_{\text{constant}} C_A^2$$

$$\int \frac{dC_A}{C_A^2} = \int (k C_{B_{0E}}^3) dt$$

$$\frac{C_A^{-1}}{-1} = -k + k C_{B_{0E}}^3 t$$

at  $t=0$   $C_A = C_{A0}$

$$k = \frac{C_{A0}^{-1} - (-1)}{(-1)}$$

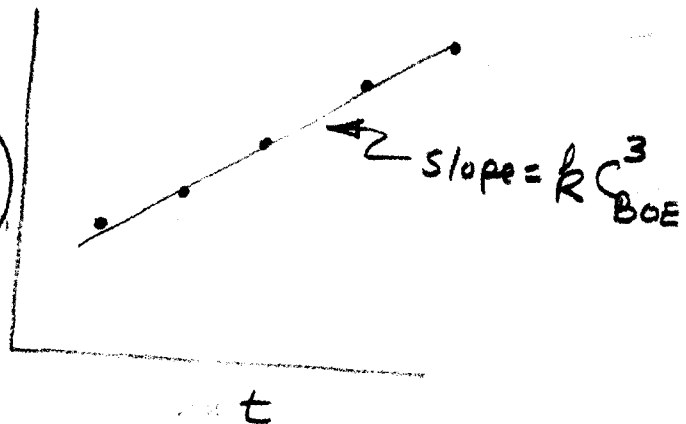
$$-C_A^{-1} + C_{A0}^{-1} = -k C_{B_{0E}}^3 t$$

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = k C_{B_{0E}}^3 t$$

Differential accentuates errors  
Integral method smooths data

Great Calculate  $k$

$$\left( \frac{1}{C_A} - \frac{1}{C_{A0}} \right)$$





## Section 5.2 Initial Rates method

### 1 Batch Reactor

$$r_A = -k C_A^\alpha$$

$$\frac{dC_A}{dt} = r_A = -k C_A^\alpha$$

$$\left. \frac{dC_A}{dt} \right|_{t=0} = -k C_{A0}^\alpha$$

minimizes the effect of a reverse reaction on your results.

2. Collect  $C_A$  vs  $t$  data at several different initial concentrations of  $C_A$ .

3. Determine  $\frac{dC_A}{dt}$

a). fit  $C_A$  vs  $t$  to a polynomial for each  $C_{A0}$  run

b) differentiate polynomial

c) calculate  $\frac{dC_A}{dt}$  at  $t=0$

4) Graph  $\ln\left(\frac{dC_A}{dt}\right)_{t=0}$  vs  $\ln C_{A0}$

based on

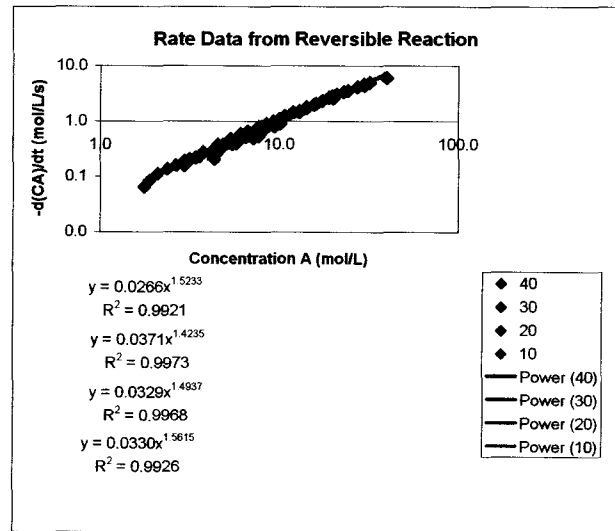
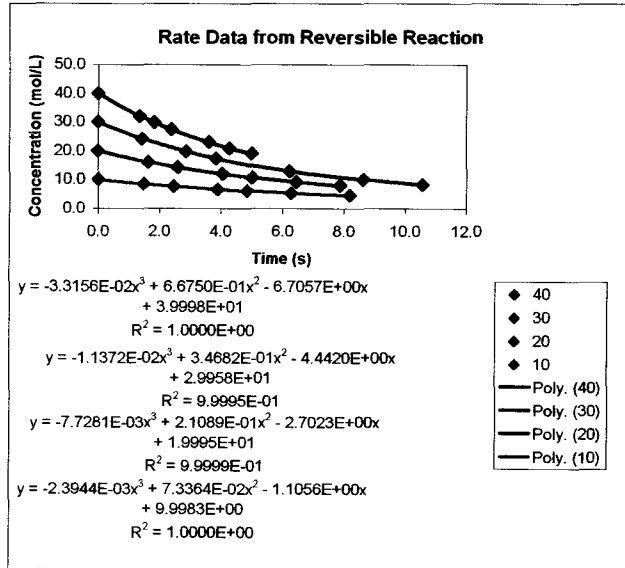
$$\ln\left(\frac{dC_A}{dt}\right)_{t=0} = \ln k + \alpha \ln C_{A0}$$

5) find  $k$  and  $\alpha$

Book example:  
Calcium metal dissolution by HCl

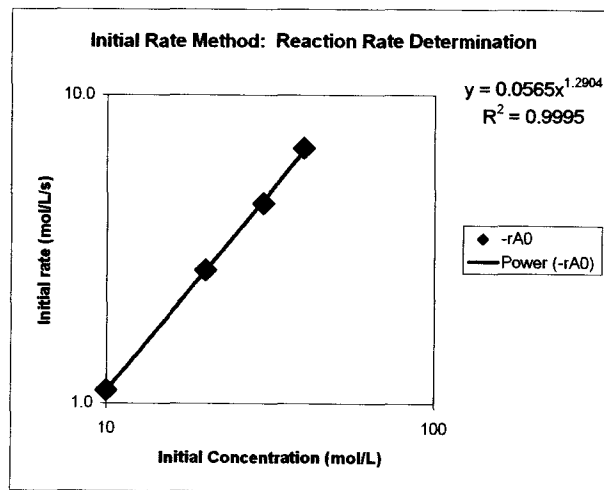
Initial Rates Method

t	CA	fit	-dCA/dt	t	CA	fit	-dCA/dt	t	CA	fit	-dCA/dt	t	CA	fit	-dCA/dt
0.0	40.0	40.0	6.7	0.0	30.0	30.0	4.4	0.0	20.0	20.0	2.7	0.0	10.0	10.00	1.11
1.3	32.1	32.1	5.1	1.4	24.2	24.3	3.5	1.6	16.1	16.2	2.1	1.5	8.5	8.51	0.90
7.4	14.3			13.4				11.2	5.9			13.0	3.2		
8.2	13.0			15.4				14.6	4.6			14.0	3.0		
10.6	10.2			15.8				16.0	4.2			15.9	2.6		
11.4	9.4			17.8				18.4	3.6			17.8	2.4		
13.8	7.7			26.9	3.2			19.4	3.4			20.2	2.1		
14.6	7.2							21.8	3.0			22.6	1.9		
17.8	5.8							22.3	3.0			24.0	1.8		
18.6	5.5							25.6	2.6			26.0	1.6		
21.8	4.7							26.6	2.5			26.4	1.6		
22.6	4.5														
23.4	4.3														
24.2	4.2														
25.8	4.0														
26.6	3.9														
27.4	3.8														

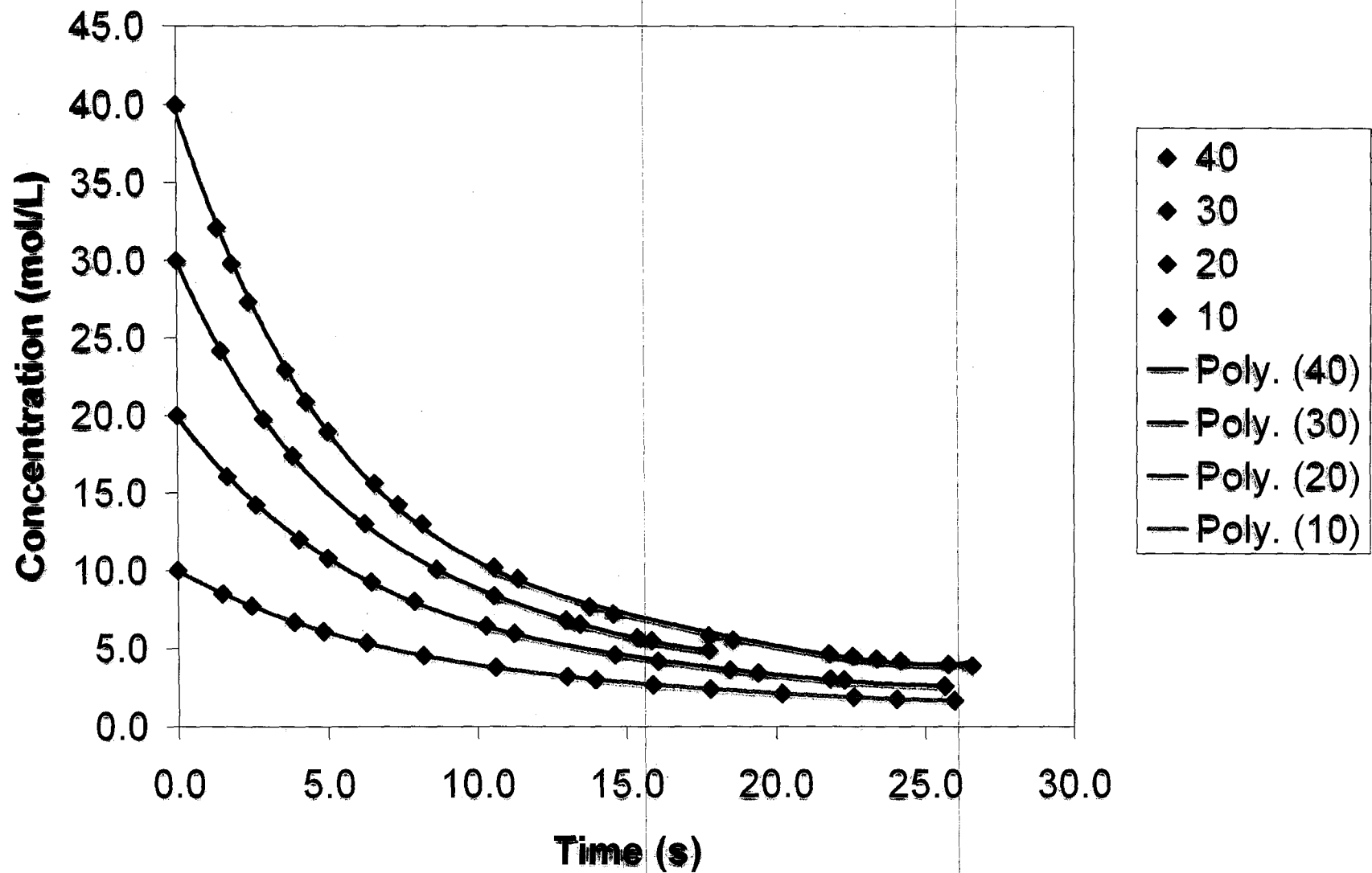


Initial rate Plot

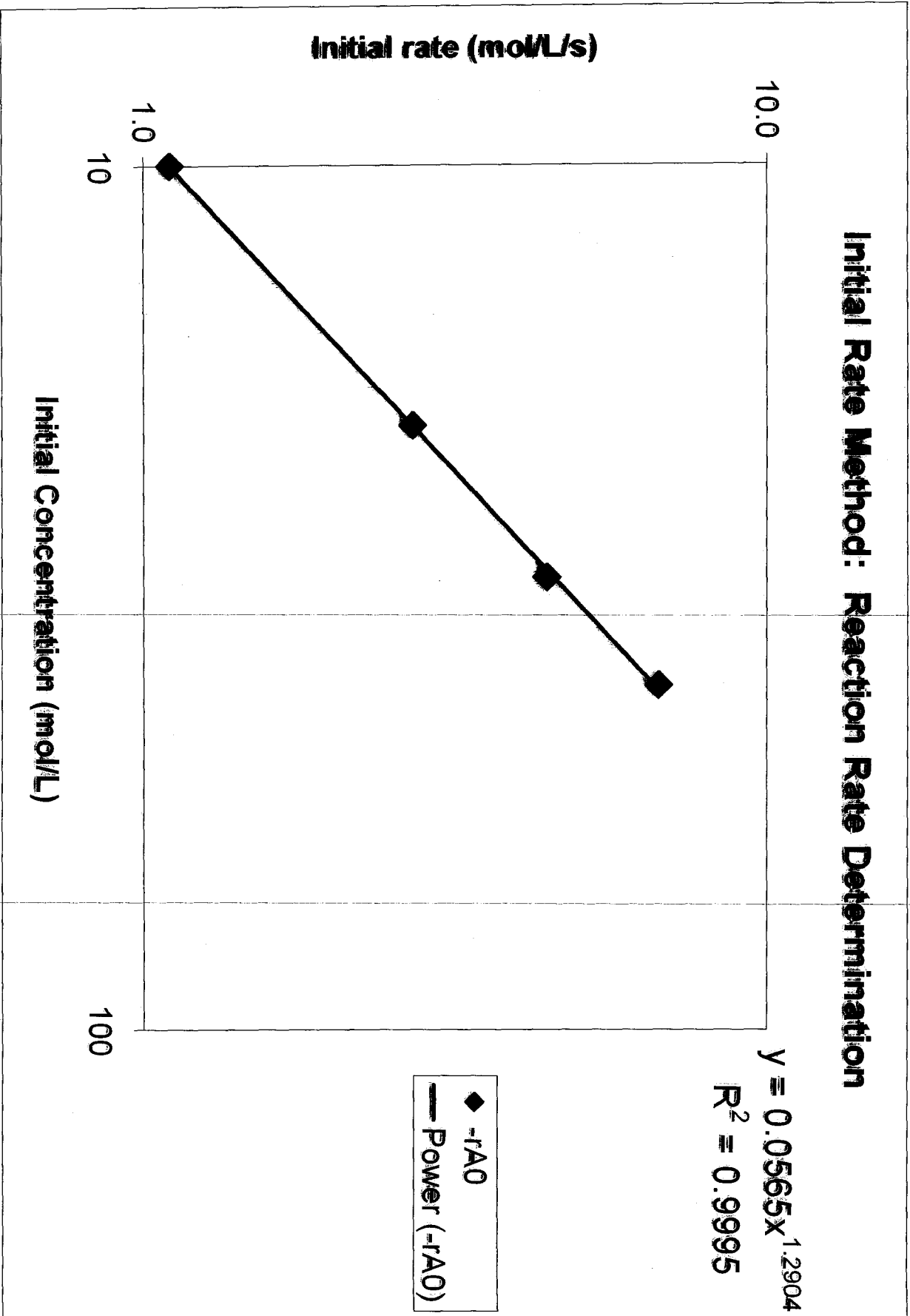
CA0	-rA0
40	6.7
30	4.4
20	2.70
10	1.11



## Rate Data from Reversible Reaction



### Initial Rate Method: Reaction Rate Determination

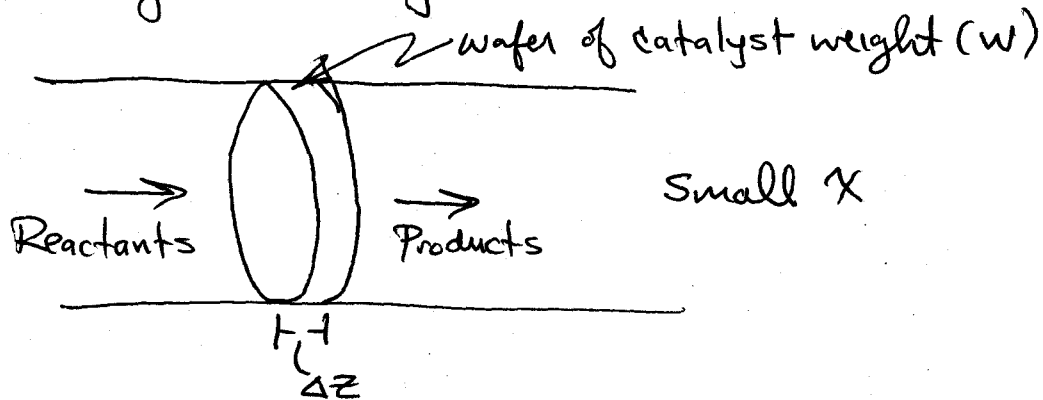




# Section ~~5.6~~ 5.4

## Differential Reactors

Heterogeneous systems



small  $X$

1) Nearly isothermal (small heat release)

2) reaction must not take place in empty tube

3) Assume no gradients  
(well-mixed)  
again!

$$\frac{\partial C_A}{\partial r} = 0 = \frac{\partial C_A}{\partial \theta}$$

4) no gas phase reactions

$$\frac{\partial C_A}{\partial t} \Delta W = F_{A0} - F_{Ae} + r_A W = 0$$

is the rate constant through the wafer  
No but

$$r_A \approx \frac{-F_{A0} + F_{Ae}}{\Delta W}$$

$$\text{for } X_A = \frac{F_{A0} - F_A}{F_{A0}}$$

$$\approx \frac{-X_A F_{A0}}{\Delta W}$$

USE METHOD OF ~~INITIAL RATES~~

# Comment on Section 5.4, 5.5

## 5.5.1

### Least-Squares Analysis

$$- \frac{dC_A}{dt} = k C_A^\alpha C_B^\beta$$

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln k + \alpha \ln C_A + \beta \ln C_B \quad \text{linearization}$$

Polymath - Regression - multiple linear  
Tools, Add-ins, Analysis ToolPak  
Choose: Regression

- 1) perform N experimental runs with A and B varied simultaneously
- 2) Repeat procedure for initial rates data - "step 3 in notes"

$$\frac{dC_A}{dt} = a + bt + ct^2 \dots$$

calculate  $\frac{dC_A}{dt}$  at  $t=0$

- 3) Tabulate data

$\left(\frac{dC_A}{dt}\right)_{t=0}$	$C_{A0}$	$C_{B0}$

fit to the following equation

$$\ln\left(\frac{dC_A}{dt}\right)_{t=0} = \text{constant} + \alpha \ln C_{A0} + \beta \ln C_{B0}$$

## 5.5.2

3.1.2 - Nonlinear least squares

- this is used when you can not linearize the mole balance.

Go Back to fixed Bed - diff Reactor 2

Go through Non-linear least-squares analysis  
Section 5.5.2

USE Polymath  
see this later

Polymath - Regression - nonlinear

22-141 50 SHEETS  
22-142 100 SHEETS  
22-144 200 SHEETS





# Laboratory Reactors and Their Limitations

Choosing the type of laboratory reactor for evaluating process kinetics may be the most crucial step in an industrial process development program. Not only would a wrong choice result in expensive delays, but data may be obtained which would scale-up erroneously, leading to a disastrous commercial design. Some of the pitfalls and limitations of various laboratory reactors are discussed for some typically complex industrial reaction systems. A modus operandi is suggested for choosing from among the potential reactors those that have the best chance of supplying the desired data. As is typical of many complex industrial reaction systems, no one reactor turns out to be ideal and many times the building of two or more types is advantageous.

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The design of an industrial reactor must begin with accurate, reliable laboratory data. For maximum usefulness these data should be derived from a carefully planned reaction kinetic study. Since the design and construction of the laboratory reactor, as well as the subsequent experimental program, can be very expensive and time consuming, close attention should be given to the type of laboratory reactor to be employed. To those fortunate enough to work in academic laboratories, it is possible to first choose a reactor type and then find a suitable reacting system to study in it. In the industrial sphere, alas, the specific reacting system is imposed on us and the problem is to search for a suitable reactor type for the kinetic studies.

Most industrial reacting systems are of sufficient complexity that a number of factors or attributes must be considered when choosing the laboratory reactor. Based on the author's industrial experience, a modus operandi is described for choosing from a wide variety of potential laboratory reactors the one with at least a fighting chance of giving the desired accurate kinetic data. To illustrate the decision process a fairly complex, but not untypical, industrial reaction system has been chosen. A number of potential laboratory reactor candidates are then considered and rated on their various attributes. Also discussed is how the reactor choices change as we relax some of the characteristics of the reaction system. The focus will be on the decision process rather than a comprehensive review of all potential laboratory reactors and their mechanical designs.

## NATURE OF REACTING SYSTEM

For the purpose of illustration we have chosen a fairly complex industrial reaction system which is not, however, untypical of industrial processes. Table 1 shows the nature of the particular reaction system chosen.

With vapor and liquid present under reacting conditions we will have three-phase flow conditions with the attendant liquid distribution and residence time problems. Our complex feedstock, consisting of many different reacting species, will present analysis and sampling problems. The particular system chosen is highly endothermic which means we will have difficulty in obtaining isothermal data. Of course, if the system were highly exothermic, we would face essentially the identical problem. Due to the highly active nature of the catalyst it will be necessary to powder it to prevent diffusion disguises. Furthermore, the same

rapid decay problem will lead to difficulties in measuring the intrinsic reaction rates. While this reaction system may seem quite complex, a large number of industrial reactions would fit this category (including exothermic reactions). One need only cite catalytic cracking, hydrocracking, and desulfurization processes in the petroleum industry to see that such a system is not untypical. In the chemical industry similar systems can be found in liquid phase oxidation and liquid phase hydrogenation processes.

In the subsequent discussion we will show how different aspects of the reacting system can be relaxed or changed and what the effect will be on the reactor choice.

## WHAT ATTRIBUTES ARE IMPORTANT?

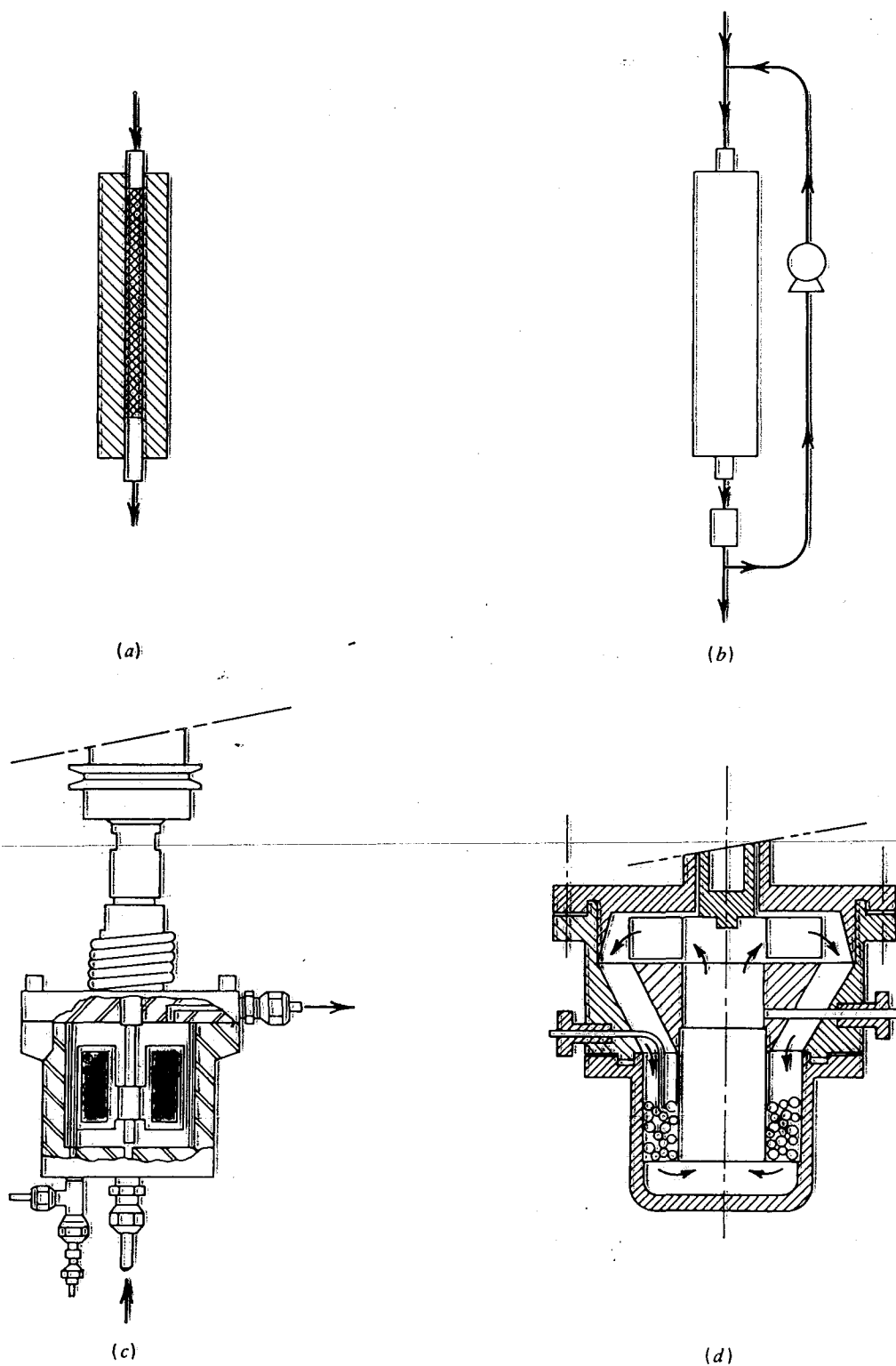
Once we have a clear understanding of the nature of our reaction system we must consider what attributes of the laboratory reactor will be important to us. Identifying the critical performance factors is probably the most crucial step in our choice of a laboratory reactor. Of course, different reacting systems may lead to different attributes. The following are the attributes which were considered important for the particular reaction system chosen:

1. Sampling and analysis of product composition
2. Isothermality
3. Residence-contact time measurement
4. Selectivity time averaging disguise
5. Construction difficulty and cost

Sampling of a two-fluid phase system containing powdered catalyst can be difficult and should be a strong consideration in the reactor design. For complex reacting systems with multiple reaction paths, it is especially critical that isothermal data be obtained. Different activation energies for the various reaction paths will make it very

TABLE 1. NATURE OF CHOSEN REACTION SYSTEM

Physical Nature of Feed:	Both vapor and liquid (wide boiling range) at reacting conditions
Chemical Nature of Feed:	Complex feed with multiple reaction paths—highly endothermic
Nature of Catalyst:	Powdered, rapidly decaying at reaction conditions, highly active
Desired:	Accurate kinetic rate data for reactor design



**Figure 2.4.1-1**

Various types of experimental reactors. (a) Tubular reactor, (b) tubular reactor with recycle, (c) spinning basket reactor, and (d) reactor with internal recycle.

difficult to unscramble the rate constants from nonisothermal data.

Because of the two-phase nature of the fluid reactants in contact with the solid phase, measurement of the true reaction times will be difficult. Differing velocities between the vapor, liquid, and solid phases must be considered in the measurement of reaction times. Adsorption of reactants on the catalyst surface may lead to catalyst-reactant contact times which are different from the fluid dynamic residence times.

Due to the decaying nature of the catalyst we will be faced with unsteady state reactor operation if the catalyst is not renewed continuously. The selectivity will be altered even for steady state reactors if different reaction paths decay at different rates (Froment and Bischoff, 1961, 1962). Thus for such a system we would find that the selectivity behavior in all reactors would become a function of catalyst decay time. For the simpler case of all reaction path activities decaying at the same rate then only an unsteady state reactor, which time averages the product, will show a selectivity disguise (Weekman, 1969). In the examples given in this paper we will assume equal decay of all catalyst functions. To eliminate the time averaging disguise one could employ rapid instantaneous measurements of the decaying system, but this can introduce sampling problems. Finally, and certainly not of least importance, we must address ourselves to the difficulty of construction and the cost of the laboratory reactor system.

We are now in a position to evaluate various potential laboratory reactors in terms of the key attributes for our particular reacting system.

#### DIFFERENTIAL REACTOR

While the differential reactor (Figure 1) gets high marks in many textbooks, it gets lower ones in the industrial lab. The main problem with the differential reactor stems from difficulties in preparing the feed composition and in the analysis of the product composition. By its nature, the differential reactor gives a small incremental conversion which can be difficult to measure for a complex multicomponent system. This limitation, of course, will depend strongly on the nature of the analysis required. One solution to the feed problem is to use an integral reactor as a feed supplier (Lunde and Kester,



Gas-Liquid, Powdered Catalyst, Decaying Catalyst System

Problem	Comments	Rating
Sampling and Analysis of Product Composition	Can be Difficult at Low Conversions	Poor-Fair
Isothermality	Low Heat Release	Fair-Good
Residence-Contact Time Measurement	Channeling Fatal V-L Distribution Problem	Fair
Selectivity Time Averaging Disguise	Transient Behavior	Poor
Construction Difficulty and Cost	One of Simplest	Good

Fig. 1. Differential reactor.



Gas-Liquid, Powdered Catalyst, Decaying Catalyst System

Problem	Comments	Rating
Sampling and Analysis of Product Composition	Normal Problems	Good
Isothermality	Very Difficult to Achieve Uniform Temperatures	Poor-Fair
Residence-Contact Time Measurement	Channeling or Liquid Distribution may be a Problem	Fair
Selectivity Time Averaging Disguise	Transient Behavior	Poor
Construction Difficulty and Cost	Fairly Straight Forward	Good

Fig. 2. Fixed bed reactor.

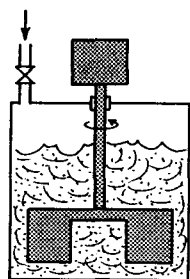
1974). Due to the small conversion, heat release, however, will be relatively small and we can give it fair marks for isothermality. Any channeling in a differential reactor will be fatal in terms of measuring accurate contact times. Being a fixed bed, good vapor-liquid distribution may be difficult and we can only give it fair marks on this attribute. Since our catalyst rapidly decays, a time-averaged selectivity disguise may be introduced which can be serious. For this reason the differential reactor is marked poor on this attribute. We can, however, give the differential reactor high marks for construction since, except for the liquid distribution problem, it can be quite simple (Pansing and Malloy, 1962).

#### FIXED BED REACTOR

We have rated the fixed bed reactor (Figure 2) good on sampling and analysis since higher conversion levels are obtained and no catalyst, product separation problems exist. However, rapid sampling to give instantaneous data during catalyst decay could present problems. The chief difficulty with the fixed bed is the problem of achieving uniform isothermal temperatures. Catalyst dilution and high heat transfer rates at the outside wall (by sand or salt bath) can help, but severely exothermic or endothermic reactions will still give significant internal bed  $\Delta T$ 's. In terms of residence time measurements, channeling or uneven liquid distribution may present problems in the fixed bed. Careful attention to distributing the liquid and gas can minimize this difficulty. As mentioned above, another problem with the fixed bed reactor is its transient nature from catalyst decay. If the product is allowed to accumulate over time, we may face a serious selectivity disguise due to the product time averaging. We can, however, give the fixed bed reactor good marks for its relatively straightforward construction and fairly low cost. Multiple taps can also be employed to give multiple conversion and selectivity points for each run (Musick et al., 1972).

### STIRRED BATCH REACTOR

Since the powdered catalyst will be dispersed as a slurry in the stirred batch reactor, separation of the product from the catalyst must be accomplished by the sampling system. It must also provide rapid quenching to prevent further reaction in the sampling system itself. For these reasons, on Figure 3, we can only give the reactor a fair rating in this respect. With enough agitation, isothermality should be excellent. Accurate residence time measurements should be possible. Since all three phases are contained in the reactor, this type could provide the most accurate measurement of contact time of all reactors considered (provided the reaction can be quenched rapidly at the end of the experiment). Unfortunately, the decaying nature of the catalyst gives us the same problems as with the fixed bed reactor; and we must give it poorer marks due to the potential selectivity disguise. On the plus side again, the stirred reactor is fairly simple to construct and the cost should be quite reasonable.



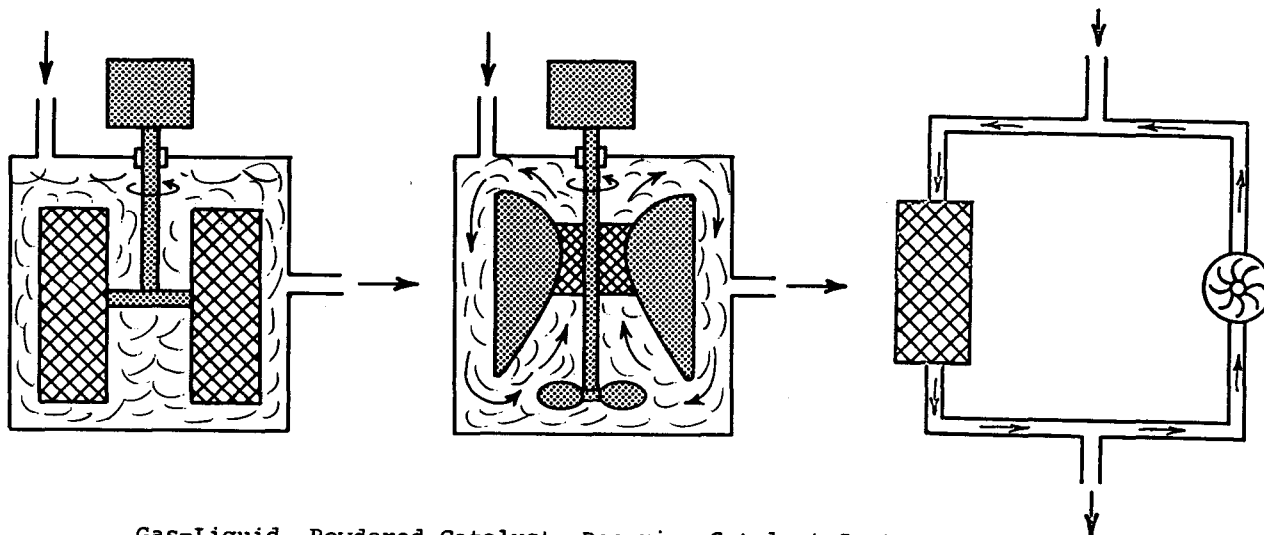
Gas-Liquid, Powdered Catalyst, Decaying Catalyst System

Problem	Comments	Rating
Sampling and Analysis of Product Composition	Difficult On-Line Analysis Problem	Fair
Isothermality	Well Mixed	Good
Residence-Contact Time Measurement	Accurate Residence Time if Rapid Quenching	Good
Selectivity Time Averaging Disguise	Transient Behavior	Poor
Construction Difficulty and Cost	Fairly Straight Forward	Good

Fig. 3. Stirred batch reactor.

### STIRRED-CONTAINED SOLIDS REACTOR

A number of different stirred-contained solids designs are equivalent in terms of performance and three are shown on Figure 4. A good review of such reactors has been given by Bennett et al. (1972). The first shown is the now (in?) famous Carberry reactor (Carberry, 1964; Tajbl et al., 1966, 1967; Tajbl, 1969a,b) where the catalyst is mounted in the paddle or agitator. For a finely



Gas-Liquid, Powdered Catalyst, Decaying Catalyst System

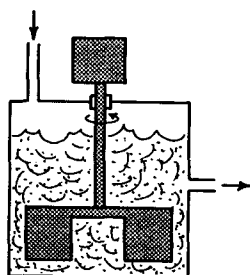
Problem	Comments	Rating
Sampling and Analysis of Product Composition	Normal Problems	Good
Isothermality	Well Mixed	Good
Residence-Contact Time Measurement	Solid Accurately Known; Gas-Vapor Known if Good Mixing	Fair-Good
Selectivity Time Averaging Disguise	Transient Behavior	Poor
Construction Difficulty and Cost	More Complex Than Batch or Fixed Bed	Fair-Good

Fig. 4. Stirred-contained solids reactor.

powdered catalyst this could present difficulties and suitable screens or containment methods would have to be devised. Next is shown the turbine reactor where a small fixed bed of catalyst is mounted at the throat of a venturi and the reacting mixture is pumped through by an impeller (Garanin et al., 1967; Brown and Bennett, 1970; Berty, 1969, 1973; Livbjerg and Valladsen, 1971; Mahoney, 1974; Choudhary and Doraiswamy, 1972). The third related type is a recirculating reactor with a fixed bed of catalyst where the reacting mixture is pumped through at a high rate, relative to the feed rate, thus achieving fully mixed conditions (Perkins and Rase, 1958; Satterfield and Roberts, 1968; Butt et al., 1962; Leinroth and Sherwood, 1964). Another variation of this type has the catalyst on the walls with a high degree of mixing from an internal impeller (Ford and Perlmutter, 1964; Relyea and Perlmutter, 1968). The sampling and analysis of the product composition of these reactors present no unusual problem since the catalyst is contained and no separation is required prior to analysis. Since with enough mixing energy all can be well mixed, isothermality should be good. The residence time of solids is, of course, accurately known and with good mixing the gas-vapor residence times can also be measured quite accurately. The worst feature of this reactor will be its unsteady state nature which can again lead to a selectivity disguise. Due to the requirements of containing the catalyst, the difficulty of construction will usually be increased over the stirred batch reactor. Some of the problems in constructing recirculating pumps have been discussed by Chambers et al. (1965) and Hanson and Benson (1973).

#### CONTINUOUS STIRRED TANK REACTOR

This reactor (Figure 5), alias the CSTR, has been the darling of the academic community for years and finds occasional use in industrial labs. As with the stirred batch reactors, the catalyst slurry in the reactor will give us some sampling difficulties, requiring either quenching or rap-



Gas-Liquid, Powdered Catalyst, Decaying Catalyst System

Problem	Comments	Rating
Sampling and Analysis of Product Composition	Catalyst-Reactant Separation Problems	Fair
Isothermality	Well Mixed	Good
Residence-Contact Time Measurement	Well Known if Good Mixing and Rapid Quenching	Fair-Good
Selectivity Time Averaging Disguise	Steady State Behavior	Good
Construction Difficulty and Cost	Difficult Catalyst Feeding and Separation Problems	Poor-Fair

Fig. 5. Continuous stirred tank reactor.



Gas-Liquid, Powdered Catalyst, Decaying Catalyst System

Problem	Comments	Rating
Sampling and Analysis of Product Composition	Rapid Catalyst-Reactant Separation Essential	Fair
Isothermality	Wall Heat Transfer Higher than Fixed Bed	Poor-Fair
Residence-Contact Time Measurement	Low Velocity Slip Problems, Higher Velocities More Accurate	Fair-Good
Selectivity Time Averaging Disguise	Steady State Operation	Good
Construction Difficulty and Cost	Fairly Straight Forward Except Isothermality	Fair-Good

Fig. 6. Straight-through transport reactor.

idly separating the catalyst from the reaction mixture. Without this provision the sample may keep reacting at different temperatures as it cools, disguising the selectivity behavior. As with the stirred batch reactor, this difficulty results in only a fair rating on the sampling attribute. Since it is well mixed we can give it high marks, however, for isothermality. If the degree of mixing is good and we can achieve rapid quenching of the exiting mixture, we can identify the contact time quite accurately. Since catalyst and reactants are added continuously it will operate in the steady state and, therefore, eliminate any possible catalyst decay selectivity disguise (at least for the case of equal decay of all catalyst functions). In constructing this reactor we can expect difficulties in accurately feeding in the slurry and in the aforementioned separation problem. For this reason we have only given it a poor-to-fair rating for construction.

#### STRAIGHT-THROUGH TRANSPORT REACTOR

In the transport reactor (Figure 6) we use either the reactant itself or an inert carrier gas to transport the catalyst through the reactor. Commercially, the transport reactor is widely employed in the catalytic cracking of heavier petroleum fractions to gasoline (Bryson et al., 1972; Strother et al., 1972; Pierce et al., 1972; Saxton and Worley, 1970). They have also found use in the drying of grains (Epstein and Mathur, 1971). Since the catalyst passes through with the reactant, it will be necessary to achieve either rapid quenching or rapid catalyst-reactant separation. As with the other dispersed or slurry catalyst reactor, this results in only a fair-to-good rating in the sampling category. While the wall heat transfer (Sadek,

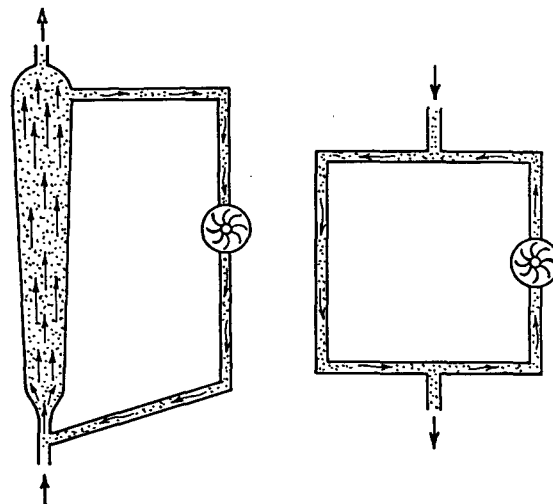
1972) will be higher than with a fixed bed reactor due to higher velocities, for highly exothermic or endothermic reactions, isothermality may still be difficult to achieve; hence, a poor-to-fair rating. For high velocities where there is little slip between the catalyst and reactant phases, we can expect very accurate measurements of residence time. At lower velocities, however, there may be slip between the phases which can lead to difficulties in accurately determining the contact time. Since the catalyst and reactant flows are continuous, we can achieve steady state operation and will not have difficulties with a time averaging disguise. The transport reactors can be quite simple, being basically a length of tubing; however, more elaborate means will be required to approach isothermality such as sand or salt baths. In addition product-catalyst separation facilities are required. Hence, the fair-to-good construction rating.

### RECIRCULATING TRANSPORT REACTOR

By adding a recirculation loop to the transport reactor we can achieve a well mixed condition provided the recirculation rate is large in comparison to the fresh feed rate (Figure 7). We will still, however, have the same problem with separating and sampling the catalyst and reactant as we had with the straight-through transport reactor. By going to the well mixed condition we have greatly improved our ability to achieve isothermality. We have also improved our contact time measurement since we can achieve higher velocities which will help eliminate catalyst-reactant slip. The operation is still steady state and we can give the recirculating transport reactor good marks in this respect. We had introduced more mechanical complexity, though, with the need for either a recirculating pump or recirculating jets. These can give plugging and flow problems in slurry systems and for this reason we have marked down the recirculating transport reactor to a fair-to-poor rating for construction. An interesting version of this reactor, containing both a reaction and regeneration zone, has recently been published (Kahney and McMinn, 1973).

### PULSE REACTOR

In the pulse reactor we have a small amount of catalyst over which we can introduce a small pulse of reactant (Figure 8). The effluent from the reactor can be fed directly to a chromatograph so as to minimize any sample handling problems. A wide range of conversion levels can be achieved so that sample analysis should not be a serious problem. A small amount of catalyst can be surrounded by a large heat sink to minimize departures from isothermality; however, again strongly exothermic or endothermic reactions can lead to significant  $\Delta T$ 's; hence the fair-to-good rating. The key difficulty with the pulse reactor lies in the fact that the catalyst surface concentrations are changing during the pulse (Makar and Merrill, 1972). Thus, the adsorbed species will change during the course of reaction which could lead to a selectivity disguise. If all reaction paths are altered identically by these adsorbed species, then the pulse reactor still could be useful for selectivity studies. Because of the hazards involved, however, we have given it a poor rating in this respect. While this is an unsteady state reactor, short pulses of reactant can follow the instantaneous behavior; fair-to-good marks are in order for this attribute. Construction difficulties will be similar to the differential reactor with a small amount of additional complexity added by the need to introduce accurate pulses of reactant. Additional problems have been reviewed by Galeski and Hightower (1970).



Gas-Liquid, Powdered Catalyst, Decaying Catalyst System

Problem	Comments	Rating
Sampling and Analysis of Product Composition	Rapid Catalyst-Reactant Separation Essential	Fair-Good
Isothermality	Well Mixed	Good
Residence-Contact Time Measurement	Well Mixed at Highly Circulating Velocities	Good
Selectivity Time Averaging Disguise	Steady State Operation	Good
Construction Difficulty and Cost	Requires Recirculating Pump or Jets	Fair-Poor

Fig. 7. Recirculating transport reactor.



Gas-Liquid, Powdered Catalyst, Decaying Catalyst System

Problem	Comments	Rating
Sampling and Analysis of Product Composition	Can Fire Direct to Chromatograph	Good
Isothermality	Small Amount of Cat. in Large Heat Sink	Fair-Good
Residence-Contact Time Measurement	Transient Surface Coverage and Chromatograph Separation	Poor
Selectivity Time Averaging Disguise	Short Pulses can Follow Instantaneous Behavior	Fair-Good
Construction Difficulty and Cost	Similar to Differential Reactor	Good

Fig. 8. Pulse reactor.

### REPRISE

Table 2 summarizes all the ratings for our given reaction system. The first thing that comes to our attention is that every one of the reactors has some poor performance feature or limitation associated with it. From this industrial researcher's experience, for most complex industrial reaction systems, clear cut winners are rare. We usually will be forced to make a trade-off between the

TABLE 2. SUMMARY OF REACTOR RATINGS  
Gas-Liquid, Powdered Catalyst, Decaying Catalyst System

Reactor type	Sampling and analysis	Isothermality	Residence-contact time	Selectivity disguise-decay	Construction problems
Differential	P-F	F-G	F	P	G
Fixed bed	G	P-F	F	P	G
Stirred batch	F	G	G	P	G
Stirred-contained solids	G	G	F-G	P	F-G
Continuous stirred tank	F	G	F-G	G	P-F
Straight-through transport	F-G	P-F	F-G	G	F-G
Recirculating transport	F-G	G	G	G	P-F
Pulse	G	F-G	P	F-G	G

G = good, F = fair, P = poor.

TABLE 3. SUMMARY OF REACTOR RATINGS  
Gas-Liquid, Powdered Catalyst, Nondecaying Catalyst System

Reactor type	Sampling and analysis	Isothermality	Residence-contact time	Selectivity disguise-decay	Construction problems
Differential	P-F	F-G	F	G	G
Fixed bed	G	P-F	F	G	G
Stirred batch	F	G	G	G	G
Stirred-contained solids	G	G	F-G	G	F-G
Continuous stirred tank	F	G	F-G	G	P-F
Straight-through transport	F-G	P-F	F-G	G	F-G
Recirculating transport	F-G	G	G	G	P-F
Pulse	G	F-G	P	G	G

G = good, F = fair, P = poor.

limitations and advantages of the various reactors. For our particular system, we can probably eliminate the differential and fixed bed as giving serious problems in isothermality or analysis. The stirred batch might be satisfactory if we could devise a rapid sampling system to obtain instantaneous data to circumvent the decay problem. Likewise, any of the stirred-contained solids reactors would be quite satisfactory if we designed an instantaneous sampling system.

Two other reactors that look quite satisfactory, except for the construction difficulties, are the old faithful CSTR and the recirculating transport reactor. Here, previous experience or reasonable ingenuity in design could overcome the sampling problem and related construction difficulties and give a most satisfactory system. The pulse reactor could be satisfactory in systems that do not strongly adsorb or where the adsorbed species do not relatively alter the reaction paths. If the reaction system is an extremely critical one involving large amounts of money, it will probably be best to build more than one type of laboratory reactor. The different reactors can then be checked against each other to give an even more reliable set of kinetic data. If the reactor results disagree, very valuable clues can arise which may lead to discovery of some important phenomena which could have been missed using a single reactor. The particular reaction system referred to in this paper was actually so important, five different type reactors were built for cross-checks; they included the fixed bed, the stirred-contained solids, the straight-through transport, recirculating transport, as well as the pulse reactor. Internal consistency checks between the reactors lead to very valuable insights into the reaction system and the subsequent scale-up problem.

#### REACTOR CHOICES FOR LESS STRINGENT REACTION SYSTEMS

We can now relax some of the reaction system conditions originally chosen and observe how the ratings of the various reactors would change.

#### Nondecaying System

With a nondecaying catalyst system all reactors would receive an equally good rating under the decay column of Table 3 since no decay selectivity disguise would occur. Now as shown on Table 3, the stirred batch and the contained-solids reactors become close competitors with the recirculating transport reactor and the CSTR. Due to the possible difficulty of rapidly separating the catalyst from the reacting mixture in the transport reactor and CSTR, the stirred batch and the contained solids get the edge as our preferred choice.

#### Single Reacting Phase

If we further relax the complexity of our reacting system by eliminating one phase, we eliminate most of the contact time problem in three of the reactors as shown on Table 4. The ratings for the contact time problem did not change for the differential and pulse reactors since the small amount of catalyst may still give bypassing problems even with single phase flow. Also the pulse reactor will still have a serious drawback if adsorbed species alter the selectivity of the reaction. While the straight-through transport reactor will still be subject to a catalyst slip problem, it may be less severe with single phase flow. For this case our top candidates are still the stirred batch and stirred-contained solids reactor.

#### Nondiffusion Limited System

If interparticle diffusion is not limiting the reaction rates, then pelleted catalysts could be used in the fixed bed and the stirred-contained solids reactors. This would simplify containing the catalyst in the latter reactor and make construction and loading simpler. It would still be desirable to use powdered catalyst for the other reactors to ensure good catalyst-reactant contacting. However, the pulse and differential reactors would be more prone to bypassing with pelleted catalyst, while the slurry type reactors would be prone to the pelleted catalyst settling out in regions of slower or uneven flow. For this nondiffusion, nondecaying system the stirred-contained solids reactor appears to be again our best choice.

TABLE 4. SUMMARY OF REACTOR RATINGS  
Single Fluid Phase, Powdered Catalyst, Nondecaying Catalyst

Reactor type	Sampling and analysis	Isothermality	Residence-contact time	Selectivity disguise-decay	Construction problems
Differential	P-F	F-G	F	G	G
Fixed bed	G	P-F	F-G	G	G
Stirred batch	F	G	G	G	G
Stirred-contained solids	G	G	G	G	F-G
Continuous stirred tank	F	G	G	G	F-G

TABLE 5. SUMMARY OF REACTOR RATINGS  
Single Fluid Phase, Nondiffusion Limited (Pelleted Catalyst), Nondecaying Catalyst, Low Heat Release System

Reactor type	Sampling and analysis	Isothermality	Residence-contact time	Selectivity disguise-decay	Construction problems
Differential	P-F	G	F	G	G
Fixed bed	G	G	F-G	G	G
Stirred batch	F	G	G	G	G
Stirred-contained solids	G	G	G	G	G
Continuous stirred tank	F	G	G	G	F-G
Straight-through transport	F-G	G	F-G	G	F-G
Recirculating transport	F-G	G	G	G	P-F
Pulse	G	G	P	G	G

G = good, F = fair, P = poor.

#### Low Heats of Reaction

If we finally relax the high heat release criterion, along with the diffusion and decay limitations, the fixed bed becomes more of a contender along with the straight-through transport reactor as shown in Table 5. Of course, the stirred-contained solids would also still be quite acceptable. The fixed bed would be the simplest reactor to construct and operate for this system provided attention was paid to preventing bypassing.

#### Special Cases

The compact moving bed reactor (Weekman and Nace, 1970; Szepe, 1972) would prove valuable if a relatively low heat release system were employed with single phase flow in a nondiffusion limited but decaying catalyst case. The compact moving bed of pellets ensures an accurate catalyst residence time with plug flow of the gas phase. Catalyst decay can be accurately measured in this steady state reactor system.

The differential reactor becomes attractive for non-decaying noncomplex reaction systems where the chemical analysis is relatively straightforward or intermediate conversion mixtures can be readily prepared.

The pulse reactor should be considered for single phase low heat release systems that either are not strongly adsorbing or where the adsorbed species do not alter the selectivity.

#### SUMMARY

The choice of a reactor for studying industrial kinetics is never a simple one; and one must sit down and rank the various reactors against the desired attributes. The final choice will likely be a compromise, but at least its limitations will be identified and can be accounted for in the subsequent experimental program.

#### LITERATURE CITED

- Bennett, C. O., M. B. Cutlip, and C. C. Yang, "Gradientless Reactors and Transient Methods in Heterogeneous Catalysis," *Chem. Eng. Sci.*, **27**, 2255 (1972).  
Berty, J. M., "Reactor for Vapor-Phase Catalytic Studies," pa-

per presented at AIChE 66th Ann. Meeting, Philadelphia (1973).

- , J. O. Hambrick, T. R. Malone, and D. S. Ullock, "Autoclave Reactor for Vapor-Phase Catalytic Studies," presented at AIChE 64th Natl. Meeting, New Orleans (1969).  
Brown, C. E., and C. O. Bennett, "Methanol Synthesis Catalysis in An Internally Recycled Reactor," *AIChE J.*, **16**, 817 (1970).  
Bryson, M. C., G. P. Huling, and W. E. Glausser, "Gulf Explores Riser Cracking," *Hydrocarbon Proc.*, **51**, 85 (May 1972).  
Butt, J. B., H. Bliss, and C. A. Walker, "Rates of Reaction in a Recycling System—Dehydration of Ethanol and Diethyl Ether Over Alumina," *AIChE J.*, **8**, 42 (1962).  
Carberry, J. J., "Designing Laboratory Catalytic Reactors," *Ind. Eng. Chem.*, **56**, 39 (1964).  
Chambers, R. P., N. A. Dougharty, and M. Boudart, "A Reliable Noncontaminating Gas Recirculation Pump," *J. Catalysis*, **4**, 625 (1965).  
Choudhary, V. R., and L. K. Doraiswamy, "Development of Continuous-Stirred Gas-Solid Reactors for Studies in Kinetics and Catalyst Evaluation," *Ind. Eng. Chem. Process Design Develop.*, **11**, 420 (1972).  
Epstein, N., and K. B. Mathur, "Heat and Mass Transfer in Spouted Beds—A Review," *Can. J. Chem. Eng.*, **49**, 467 (1971).  
Ford, F. E., and D. D. Perlmutter, "The Kinetics of the Brass-Catalysed Dehydrogenation of Sec-Butyl Alcohol," *Chem. Eng. Sci.*, **19**, 371 (1964).  
Froment, G. F., and K. B. Bischoff, "Non-Steady State Behavior of Fixed Bed Catalytic Reactors due to Catalyst Fouling," *ibid.*, **16**, 189 (1961).  
—, and K. B. Bischoff, "Kinetic Data and Product Distributions from Fixed Bed Catalytic Reactors Subject to Catalyst Fouling," *ibid.*, **17**, 105 (1962).  
Galeski, J. B., and J. W. Hightower, "Microcatalytic Reactors: Kinetics and Mechanisms with Isotopic Tracers," *Can. J. Chem. Eng.*, **48**, 151 (1970).  
Garanin, V. I., U. M. Kirkchi, and K. M. Minachev, "A Gradientless Reactor for Studying the Kinetics of Reactions Proceeding Under Pressure," *Kinetics Catal. (USSR) (Trans.)*, **8**, 605 (1967).  
Hanson, F. V., and J. E. Benson, "An Inexpensive Noncontaminating Gas Recirculation Pump," *J. Catalysis*, **31**, 471 (1973).  
Kahney, R. H., and T. D. McMinn, "Laboratory Transported Bed Reactors," paper presented at AIChE 66th Ann. Meet-



- ing, Philadelphia (1973).
- Leinroth, J. P., and T. K. Sherwood, "Semibatch Operation of a Recirculation Reactor for the Hydrogenation of Ethylene," *AICHE J.*, **10**, 524 (1964).
- Livbjerg, H., and J. Valladsen, "Internal Recirculation Reactor for the Oxidation of Sulphur Dioxide on Vanadium Catalysts," *Chem. Eng. Sci.*, **26**, 1495 (1971).
- Lunde, P. J., and F. L. Kester, "Carbon Dioxide Methanation on a Ruthenium Catalyst," *Ind. Eng. Chem. Process Design Develop.*, **13**, 27 (1974).
- Mahoney, J. A., "The Use of a Gradientless Reactor in Petroleum Reaction Engineering Studies," *J. Catalysis*, **32**, 247 (1974).
- Makar, K., and R. P. Merrill, "Rate Coefficients from Pulsed Microcatalytic Reactors—Nonlinear Kinetics with Linear Isotherms," *ibid.*, **24**, 546 (1972).
- Musick, J. K., F. S. Thomas, and J. E. Johnson, "Catalytic Oxidation Studies in the Vapor Phase Using Axial Sampling of the Bed," *Ind. Eng. Chem. Process Design Develop.*, **11**, 350 (1972).
- Pansing, W. F., and J. B. Malloy, "A Differential Reactor System," *Chem. Eng. Progr.*, **58**(12), 53 (1962).
- Perkins, T. K., and H. F. Rase, "An Improved Experimental Reactor for Applied Kinetic Studies," *AICHE J.*, **4**, 351 (1958).
- Pierce, W. L., R. P. Souther, T. G. Kaufman, and D. F. Ryan, "Innovations in Flexicracking," *Hydrocarbon Proc.*, **51**, 92 (May, 1972).
- Relyea, D. L., and D. D. Perlmutter, "A Stirred Reactor with Porous Catalyst Wall," *Ind. Eng. Chem. Process Design Develop.*, **7**, 261 (1968).
- Sadek, S. E., "Heat Transfer to Air-Solids Suspensions in Turbulent Flow," *ibid.*, **11**, 133 (1972).
- Satterfield, C. N., and G. W. Roberts, "Kinetics of Thiophene Hydrogenolysis on a Cobalt Molybdate Catalyst," *AICHE J.*, **14**, 159 (1968).
- Saxton, A. L., and A. C. Worley, "Modern Catalytic-Cracking Design," *Oil Gas J.*, **68**(20), 82 (1970).
- Strother, C. W., W. L. Vermillion, and A. J. Conner, "Riser Cracking Gives Advantages," *Hydrocarbon Proc.*, **51**, 89 (May 1972).
- Szepe, S., "Concurrent and Countercurrent Moving Bed Reactors," *Adv. Chem. Ser.*, **109**, 510 (1972).
- Tajbl, D. G., J. B. Simons, and J. J. Carberry, "Heterogeneous Catalysis in a Continuous Stirred Tank Reactor," *Ind. Eng. Chem. Fundamentals*, **5**, 171 (1966).
- \_\_\_\_\_, H. L. Feldkerchner, and A. L. Lee, "Cleanup Methanation for Hydrogasification Process," *Adv. Chem. Ser.*, **69**, 166 (1967).
- \_\_\_\_\_, "Kinetics of Catalytic Ethane Hydrogenolysis: Stirred Reactor Study of Commercial Nickel Catalyst," *Can. J. Chem. Eng.*, **47**, 154 (1969).
- \_\_\_\_\_, "Hydrogenolysis of Ethane and of Propane Over a Commercial Ruthenium Catalyst," *Ind. Eng. Chem. Process Design Develop.*, **8**, 364 (1969).
- Weekman, V. W., Jr., "Kinetics and Dynamics of Catalytic Cracking Selectivity in Fixed-Bed Reactors," *ibid.*, **8**, 385 (1969).
- \_\_\_\_\_, and D. M. Nace, "Kinetics of Catalytic Cracking Selectivity in Fixed, Moving, and Fluid Bed Reactors," *AICHE J.*, **16**, 397 (1970).

#### THE AUTHOR

V. W. Weekman, Jr. has been with Mobil Research and Development Corporation since his M.S. ChE at Michigan (1954), including a few years as a Mobil Fellow to obtain his Ph.D. in Chemical Engineering at Purdue (1963). He mentions his earlier career was tempered by the experience of operating laboratory pilot and bench scale units, followed by the chastening experience of interpreting kinetically such data, while in recent years he has had the thoroughly humbling experience of trying to explain commercial reactor behavior based on known and unknown principles. He is currently Manager of Systems Research. At other times he can be found sailing his ketch in the Chesapeake (with occasional Atlantic forays) with an enthusiasm which he ranks slightly below the level of irrational fanatic.

## Iron Oxide Sorbents for Regenerative Sorption of $\text{NO}_x$

Supported ferric oxide can remove oxides of nitrogen from hot and cold gases, 20°C to 350°C, containing NO in the range of 50 to 1000 ppm when sufficient oxygen is present. Rates of sorption and capacities increase with oxygen concentration. The sorbent can be regenerated with air at 400° to 450°C an indefinite number of times.

Reduced iron oxide sorbs nitric oxide more rapidly than the ferric oxide and has a higher capacity. It can be regenerated with hot reducing gases.

LINUS LEUNG  
and  
DIMITRI GIDASPOW

Institute of Gas Technology  
Chicago, Illinois 60616

#### SCOPE

Combustion of a fuel in air results in the formation of small but potentially harmful concentration of nitric oxide. To remove this air pollutant from flue gases and exhaust an effective sorbent is needed.

To estimate the size of potential sorbers from laboratory data it is desirable to obtain differential rate data.

Such kinetic data are required for an estimate of the size of a rotary type sorber in which the sorbent is continuously regenerated (Gidaspow and Onischak, 1973). For the design of the more conventional fixed bed sorbers, capacity data is needed. Capacity data can be obtained from integrating the time dependent differential rate data.

TABLE 5-2. SUMMARY OF REACTOR RATINGS:<sup>a</sup> GAS-LIQUID, POWDERED CATALYST, DECAYING CATALYST SYSTEM

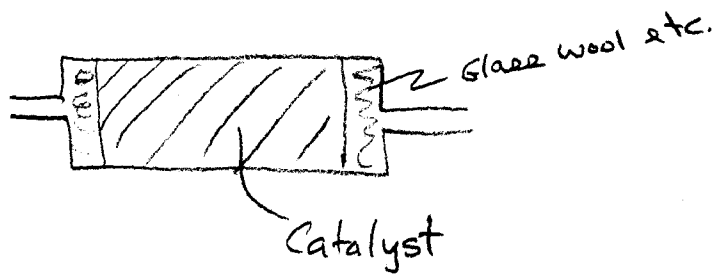
<i>Reactor Type</i>	<i>Sampling and Analysis</i>	<i>Isothermality</i>	<i>Fluid-Solid Contact</i>	<i>Decaying Catalyst</i>	<i>Ease of Construction</i>
Differential	P-F	F-G	F	P	G
Fixed bed	G	P-F	F	P	G
Stirred batch	F	G	G	P	G
Stirred-contained solids	G	G	F-G	P	F-G
Continuous-stirred tank	F	G	F-G	F-G	P-F
Straight-through transport	F-G	P-F	F-G	G	F-G
Recirculating transport	F-G	G	G	F-G	P-F
Pulse	G	F-G	P	F-G	G

<sup>a</sup>G, good; F, fair; P, poor.

I

# Fixed BED REACTOR

5-9

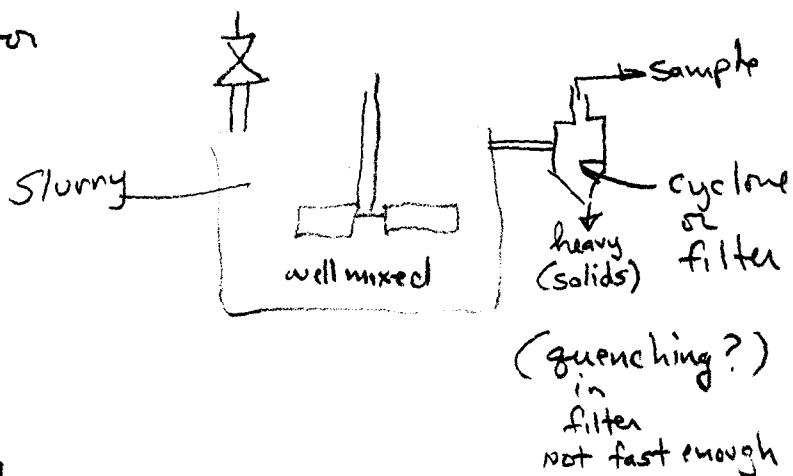


~~Stavits~~  
 10/11/90  
 10/11/90

- 1) More product formed than diff
- 2) If  $r$  has high  $\phi$  (Endo or Exo) problems (not gradient less)
- 3) catalyst decay
- 4) cheap

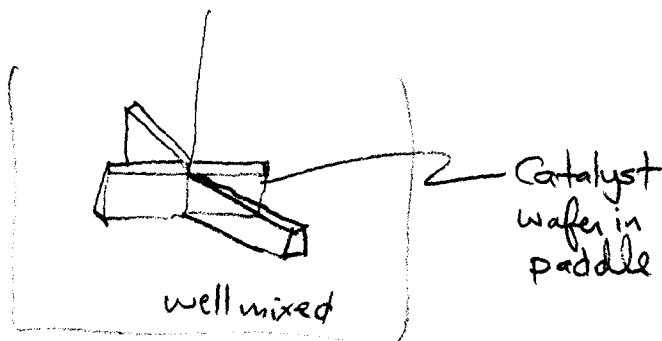
II

## Stirred batch Reactor



## III stirred contained solids Reactor (Basket-type)

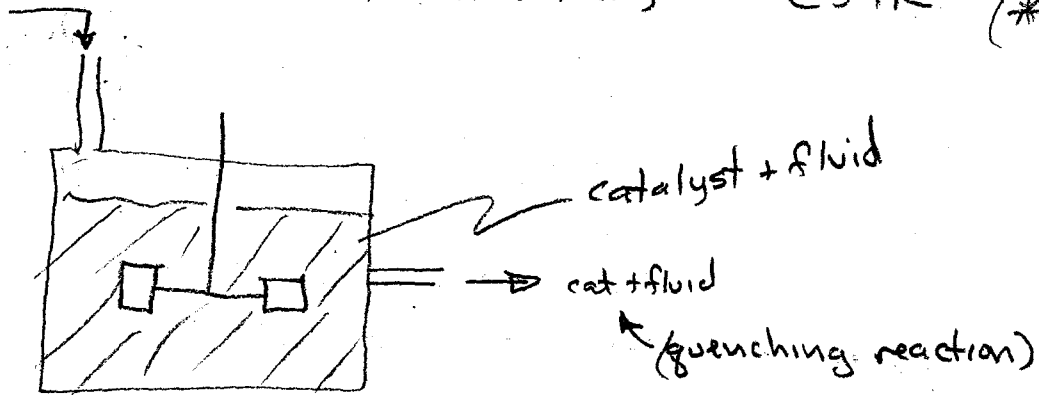
minimize external m. T.  
 (Containment of particles  
 in screen  
 -construction (F-G)  
 (Catalyst decay  
 problems)



IV

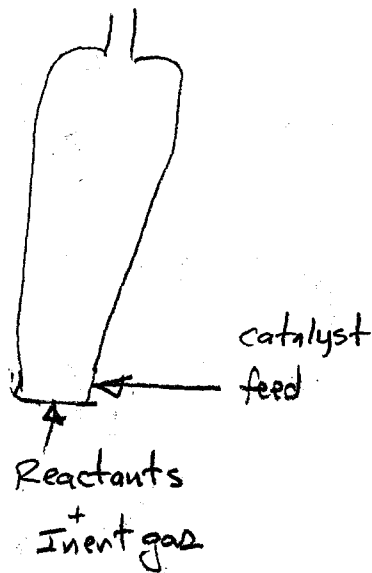
cat + feed slurry (Difficult to feed)

CSTR (\*\*\*) -5-60



Catalytic activity is constant

V Straight through transport R



- 1) No cat. decay
- 2) Not Isothermal
- 3) Gas-cat. slip  $\bar{T}$  different for cat and prod.
- 4) quenching

VI Add recycle (Recirculating Trans Reactor) (\*\*\*)

- 1) high cost in const.
- 2) Catalyst decay

- 1) CSTR + Recirc. Activity
- 2) If catalyst does not decay stirred batch and contained solids  $\rightarrow$  good
- 3) fixed bed - No cat A. decay, isothermal rxn

### 5.6.7 Summary of reactor ratings

The ratings of the various reactors are summarized in Table 5-2. From this table one notes that the CSTR and the recirculating transport reactor appear to be the best choices, since they are satisfactory in every category except for construction.<sup>†</sup> However, if the catalyst under study does not decay, the stirred batch and contained solids reactors appear to be the best choices. If the system is not limited by internal diffusion in the catalyst pellet, larger pellets could be used and the stirred-contained solids is the better choice. If the catalyst is nondecaying and heat effects are negligible, the fixed-bed (integral) reactor would be the top choice, owing to its ease of construction and operation. However, in practice, usually *more than one* reactor type is used in determining the reaction-rate-law parameters.

TABLE 5-2. SUMMARY OF REACTOR RATINGS:<sup>a</sup> GAS-LIQUID, POWDERED CATALYST, DECAYING CATALYST SYSTEM

<i>Reactor Type</i>	<i>Sampling and Analysis</i>	<i>Isothermality</i>	<i>Fluid-Solid Contact</i>	<i>Decaying Catalyst</i>	<i>Ease of Construction</i>
Differential	P-F	F-G	F	P	G
Fixed bed	G	P-F	F	P	G
Stirred batch	F	G	G	P	G
Stirred-contained solids	G	G	F-G	P	F-G
Continuous-stirred tank	F	G	F-G	F-G	P-F
Straight-through transport	F-G	P-F	F-G	G	F-G
Recirculating transport	F-G	G	G	F-G	P-F
Pulse	G	F-G	P	F-G	G

<sup>a</sup>G, good; F, fair; P, poor.

## 5.7 Experimental Design

In the preceding pages of this chapter various methods of analyzing rate data have been presented. It is just as important to know in which circumstances to use each method as it is to know the mechanics of these methods.

### 5.7.1 Finding the rate law

A chart that may aid you in deciding the type of experimental plan to follow is presented in Figure 5-14. This chart applies primarily to isothermal batch reaction systems in which only one chemical reaction is taking place.

As level 1 on the chart shows, when the reaction rate law is known, the integral method of analysis may be used after performing an experiment to determine

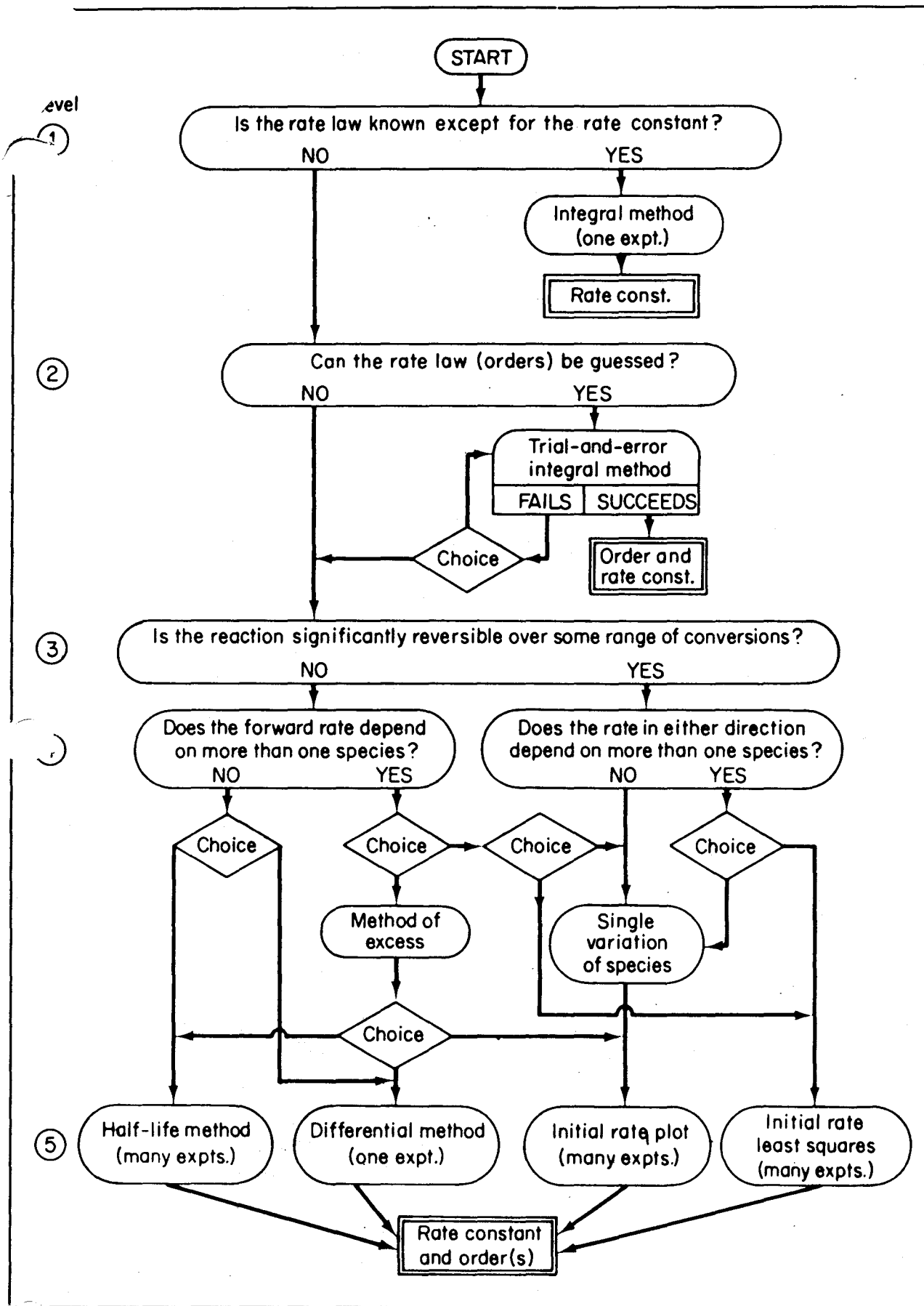


Figure 5-14 Interpretation of rate data. (From R. L. Curl, unpublished notes, University of Michigan, Ann Arbor.)