Experimental Search for a Simple Rate Equation to Describe Deactivating Porous Catalyst Particles

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This paper concerns the experimental determination of the orders of reaction and deactivation in the $n$th order rate equation which represents the four broad classes of deactivation of catalyst particles: parallel, series, side-by-side, and independent. We discuss the various reactor types which may be used, both batch-solids and flowing solids. For batch-solids systems we show that when deactivation is concentration independent then using a batch of fluid or any flow of fluid gives results which are simple to interpret. However, when deactivation is concentration dependent then only one very particular form of contacting is recommended in that it alone allows decoupling of concentration and activity effects, and their study one at a time.

In essence we show how the methods for $n$th order homogeneous reactions can be extended in a simple way to catalytic systems with deactivating porous solids.

**Nomenclature**

- $a =$ activity of a catalyst pellet, defined in Eq. 3
- $A =$ gas phase reactant
- $C =$ concentration (mol/liter)
- $d =$ order of deactivation, see Eqs. 4–8
- $F_{A0} =$ feed rate of reactant $A$ (mol/sec)
- $k =$ rate constant for the reaction of $A$, see Eqs. 4–8 (liter$^n$/mol$^{n-1}$-sec-g catalyst)
- $k'$, $k'' =$ rate constant for the deactivation reaction, see Eqs. 4–8 (liter$^{n'}$/sec-mol$^{n''}$)
- $k_d' = k_d C_A^{n''}$
- $n =$ reaction order for conversion of reactant $A$
- $n'' =$ order of concentration dependency of the deactivation
- $N_A =$ moles of $A$ (mol)
- $P =$ poison
- $-r_A' =$ rate of reaction of $A$ (mol/sec-g catalyst)
- $R =$ product of reaction of $A$
- $t =$ time (sec)
- $T =$ temperature ($^\circ$K)
- $V =$ volume of fluid (liters)
- $W =$ weight of catalyst (g)
- $X_A =$ fractional conversion of reactant $A$
- $\epsilon_A =$ fractional change in a volume of an element of reactant fluid on complete conversion
- $\tau' = \frac{W C_{A0}}{F_{A0}}$, capacity factor of a reactor called the weight-time (g cat-sec/liter of fluid)
- $0 =$ initial time, or for fresh catalyst
- $\infty =$ at infinite time

**Greek letters**

- $\xi =$ poison following properties:
  1. It should be general enough to represent the various types of deactivation encountered in practice.
  2. Its parameters should be related in a...
simple way with the mechanisms of action of the deactivation.
3. Its form should be such that its parameters can be found directly by experiment.
4. Its form should be useful for those concerned with reactor design. Thus, the equation must be easy to use to predict performance of reactors, optimum operating schedules, etc.

A recently proposed form of kinetic equation gives promise to satisfy these requirements. Its general form for the rate of disappearance of any reactant \( A \) in the environs of a representative pellet of catalyst is given by

\[
-r'_{A} = f_{i}(\text{conditions of the fluid bathing the pellet of catalyst}) \cdot f_{p}(\text{present activity of the catalyst pellet})
\]

Coupled with this expression, the rate at which the activity of the pellet decreases with time is written as

\[
-w_{A} = f_{i}(\text{conditions of the fluid bathing the pellet of catalyst}) \cdot f_{p}(\text{present state of the catalyst pellet})
\]

where the activity of the pellet at any time is defined as

\[
a = \text{rate at which the pellet converts reactant } A \text{ with a fresh pellet} = \frac{-r'_{A}}{-r'_{A_{s}}}
\]

The activity starts at unity and usually drops smoothly with time to zero.

Let us illustrate this formulation by using nth order kinetics with the four major types of deactivation. Thus, if the material which deposits on the surface to cause it to lose its activity is called the poison \( P \), we have:

**Parallel deactivation** in which reactant decomposes to produce the poison

\[
A \rightarrow R \quad -r'_{A} = kC_{A}^{n}a \\
A \rightarrow P \quad -\frac{da}{dt} = k_{d}C_{A}^{n}a^{d}
\]

**Series deactivation** in which product decomposes to produce the poison

\[
A \rightarrow R \quad -r'_{A} = kC_{A}^{n}a \\
-\frac{da}{dt} = k_{d}C_{R}^{n}a^{d}
\]

**Side-by-side deactivation**, representative of feeds which contain poisonous impurities

\[
A \rightarrow R \quad -r'_{A} = kC_{A}^{n}a \\
P \rightarrow P \quad -\frac{da}{dt} = k_{d}C_{R}^{n}a^{d}
\]

\[
A \rightarrow R \quad -r'_{A} = kC_{A}^{n}a
\]

\[
-\frac{da}{dt} = k_{d}a^{d}
\]

**Independent deactivation**, a result of structural modifications or sintering of the catalyst surface which is exposed to extreme conditions, and so called because the decay is unaffected by the concentration of materials in the gas stream but is dependent on the length of time spent in the high temperature environment

\[
-r'_{A} = kC_{A}^{n}a
\]

\[
-\frac{da}{dt} = k_{d}a^{d}
\]

In certain reactions, such as isomerizations and cracking, deactivation may be caused both by reactant and product, or

\[
A \rightarrow R, P \quad -r'_{A} = k_{p}C_{A}^{n}a, k_{d}C_{R}^{n}a^{d}
\]

**Coupled deactivation**, in which both reactant and product decompose to produce poison

\[
A \rightarrow R \quad -r'_{A} = kC_{A}^{n}a \\
R \rightarrow P \quad -\frac{da}{dt} = k_{d}C_{R}^{n}a^{d}
\]

In the above expressions the constants \( n, n', \text{ and } d \) are the orders of reaction and of deactivation. The rate constants \( k \) and \( k_{d} \) are normally taken to be Arrhenius temperature dependent

\[
k = k_{0}e^{-E/kT} \quad \text{and} \quad k_{d} = k_{0d}e^{-E_{d}/kT},
\]

where \( E \) and \( E_{d} \) are the activation energies of the main reaction and of the deactivation.

However, since \( C_{A} + C_{R} \) remains constant for a specific feed, this type of deactivation reduces to the simple-to-treat independent deactivation of Eq. 7.

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Let us now turn to the status of this formulation with respect to the above-mentioned four properties of a desirable rate form. First Szep (1) has shown that this form generalizes many of the previously proposed kinetic equations for deactivating catalyst pellets: the linear, ex-
ponential, hyperbolic, Voorhies, Elovich, and others (property 1). In addition preliminary studies by Khang (2) indicate that in many cases this formulation is related to the mechanisms of deactivation, accounting for pore diffusion effects without particular difficulty (property 2). Finally, in recent years numerous studies, referred to in Levenspiel (3) have uncovered the fact that this formulation is eminently suitable for reactor design purposes, allowing simple analytical solution to optimal scheduling problems for maximizing conversion and yield. Such problems have been impossible to solve with other equation forms (property 4).

As yet no one has examined how well this form of kinetic equation satisfies the third property, a desirable rate form. This is the aim of this paper.

This paper shows how the parameters of this formulation, \( n, n', d, k, k_d, E, E_d \) can be found directly by experiment. Note that for any condition of operations the values of these parameters will account not only for the intrinsic surface kinetics, but also for pellet size and geometry, as well as pore diffusion effects for both reactants and poisons.

We illustrate the search strategy by comparison with the simple and well known homogeneous reaction. There the rate is dependent on two factors, the temperature and composition, and these dependencies are normally determined one at a time in separate experiments. Different rate forms are guessed at, starting with the very simplest, first order, second order, and so on, until a reasonable match between the rate form and experiment is obtained. The experiments themselves are usually conducted in a batch reactor and are analyzed either by differential analysis (direct test with experiment of the differential rate expression) or by integral analysis (integration of the guessed differential rate expression and a test of the resulting expression with experiment).

Now in catalytic systems with deactivating catalysts matters are somewhat more complicated since we have three independent factors to contend with: the temperature, composition, and activity of the catalyst pellet, and many more parameters to evaluate. Nevertheless, by proper choice of reactor type and design of experiment it becomes possible to directly evaluate and test rate equations of various kinds, just as with homogeneous systems.

**Batch-Solids vs Flowing Solids**

**Experimental Reactors**

First, the available experimental devices fall into two broad groups, those which use a fixed batch of catalyst, and those which use a flow of particles through the reactor, see Fig. 1.

Because of the ease of experimentation the setups which use a fixed batch of solids are much preferred, however these can only be used when deactivation is slow enough so that the changing fluid concentration can be followed for a sufficiently long time before exhaustion of the catalyst. Deactivation in the order of minutes or longer can use the fixed batch of solids.

Whenever deactivation is very rapid, in the order of seconds or less, then a flowing-solids system must be used. Cracking catalysts whose activity half-life is in the order of 0.1–1 sec fall into this category.

This paper is primarily concerned with the batch-solids reactor. Here the choice of convenient reactor type again splits into two classes depending on whether the deactivation expressions \( \frac{da}{dt} \) of Eqs. 4–7 are concentration dependent or not. When concentration independent (or \( n' = 0 \)) then any type of batch-solids system may be used; but when concentration dependent, then unless one particular type of reactor is used the analysis of the experimental results becomes awkward and difficult.

We treat these two classes of rate equation in turn.

**Batch-Solids: Finding the Rate Equation when the Deactivation is Independent of Concentrations**

Let us illustrate how to interpret experiments from the various batch-solids reactors of Fig. 1, how to manipulate the basic performance equations for these reactors by testing the fit for the simplest
rate expression for deactivating catalyst particles, or

\[
A \rightarrow R \quad -r'_{A} = k_{A}a \quad \text{ (9a)}
\]

\[-\frac{da}{dt} = k_{d}a. \quad \text{ (9b)}
\]

This represents first-order reaction and first-order deactivation which in addition is concentration independent.

**Batch-solids, batch-fluid (Fig. 1a).** Here we need to develop an expression to relate the changing concentration of gaseous reactant with time. Using time as the one independent variable throughout the run, the kinetic expressions of Eq. 9 become

\[
-\frac{dC_{A}}{dt} = \frac{W}{V} \left( - \frac{1}{W} \frac{dN_{A}}{dt} \right)
\]

\[= \frac{W}{V} (-r'_{A}) = \left( \frac{kW}{V} \right) C_{A0}a = k'' a C_{A}, \quad \text{ (10)}
\]

and

\[-\frac{da}{dt} = k_{d}a. \quad \text{ (11)}
\]

Integrating Eq. 11 yields

\[a = a_{0}e^{-k'd}, \]

and for initial activity of unity, or \[a_{0} = 1,\]

we find

\[a = e^{-k'd}. \quad \text{ (12)}
\]

Replacing Eq. 12 in Eq. 10 gives

\[-\frac{dC_{A}}{dt} = k'' e^{-k'd}C_{A},
\]

which on separation and integration gives

\[\ln \frac{C_{A0}}{C_{A}} = \frac{k''}{k_{d}} [1 - e^{-k'd}]. \quad \text{ (13)}
\]

This expression shows that even at infinite time the concentration of reactant in an irreversible reaction does not drop to zero but is governed by the rates of reaction and deactivation, or

\[\ln \frac{C_{A0}}{C_{A\infty}} = \frac{k''}{k_{d}} \quad \text{ (14)}
\]

Combining the above two expressions and rearranging gives the useful expression

\[\ln \ln \frac{C_{A}}{C_{A\infty}} = \ln \ln \frac{C_{A0}}{C_{A\infty}} - k_{d}t. \quad \text{ (15)}
\]

The plot of Fig. 2 shows how to test for this rate form.

The batch reactor is a practical and useful device when the characteristic times for reaction and deactivation are of the same order of magnitude. This factor can be controlled by the experimenter by proper choice of \(W/V\). If deactivation is much
slower than the conversion, then $C_{A0}$ becomes very low and difficult to measure accurately.

**Batch-solids: Completely mixed fluid of constant flow rate** (Fig. 1c). Inserting the rate equation of Eq. 9a into the performance expression for a completely mixed flow reactor gives

$$\frac{W}{F_{A0}} = x_A - \frac{x_A}{kaC_A},$$

(16)

and on rearrangement

$$\frac{C_{A0}}{C_A} = 1 + k\alpha \left( \frac{WC_{A0}}{F_{A0}} \right) = 1 + k\alpha \tau',$$

(17)

where $\tau'$ is a capacity factor analogous to space-time and called the weight-time.

In this expression the activity varies with chronological time. To eliminate this quantity integrate Eq. 9b (see Eq. 12) and insert into Eq. 17. This gives

$$\frac{C_{A0}}{C_A} = 1 + k\alpha e^{-k\alpha \tau'},$$

(18)

which on rearrangement gives in more useful form

$$\ln \left( \frac{C_{A0}}{C_A} - 1 \right) = \ln(k\tau') - k_{dL}.$$

(19)

This expression shows how the reactant concentration at the reactor outlet rises with time, and the plot of Fig. 3 provides the test of this kinetic equation. If the data fall on a straight line then the slope and intercept yield the two rate constants of Eq. 9.

We should mention that this and the following derivations for a batch of solids are based on the pseudo-steady-state assumption which views that conditions change slowly enough with time so that the system can be considered to be at steady state at any instant. Since a batch of solids can only be used in experimentation if deactivation is not too rapid this assumption is reasonable.

**Batch-solids: Plug constant flow of fluid** (Fig. 1b). Here the performance expression combined with the rate of Eq. 9a gives

$$\frac{W}{F_{A0}} = \int_0^{x_A} \frac{dX_A}{-\tau'_A} = \int_0^{x_A} \frac{dX_A}{kaC_A},$$

(20)

Integrating and replacing $a$ by Eq. 12 gives

$$\frac{W}{F_{A0}} = \tau' = \frac{1}{ka} \ln \left( \frac{C_{A0}}{C_A} \right) = \frac{1}{ke^{-k\alpha \tau'}} \ln \left( \frac{C_{A0}}{C_A} \right),$$

(21)

which becomes on rearrangement

$$\ln \left( \frac{C_{A0}}{C_A} \right) = \ln(k\tau') - k_{dL}.$$

(22)

Figure 4 shows how to test for the kinetics of Eq. 9 and evaluate the rate constants for Eq. 9 from this type of reactor.

**Batch-solids: Completely mixed fluid with changing flow rate so as to keep $C_A$ constant** (Fig. 1c). As we shall see it is often extremely useful to take kinetic data at a fixed reactant concentration level. This
is done with deactivating catalysts by properly adjusting the feed rate.

At any instant in the completely mixed reactor we already have found from Eq. 18 that

\[ \frac{C_A^0}{C_A} = 1 + ke^{-kd\tau'}. \]

To keep \( C_A \) constant the flow rate must be lowered continually, hence the variables in this situation are \( \tau' \) and \( t \). So, on rearranging we obtain

\[ \ln \tau' = kd + \ln \left( \frac{C_A^0 - C_A}{kC_A} \right). \quad (23) \]

Figure 5 shows how to test for the kinetic form of Eq. 9 with this varying flow procedure.

Actually there is no particular advantage to using varying flow over constant flow when testing for the kinetics of Eq. 9 or any other concentration independent deactivation. However for testing rate equations where the deactivation is concentration dependent this procedure is by far the most useful because it allows decoupling the three factors of concentration, temperature, and activity, and their study one at a time.

**Batch-solids: Plug changing flow of fluid so as to keep \( C_A,_{out} \) constant (Fig. 1b).** At any instant in the plug flow reactor Eq. 21 applies. Also noting that \( \tau' \) and \( t \) are the two variables we obtain on suitable rearrangement

\[ \ln \tau' = kd + \ln \left( \frac{1}{kd} \ln \frac{C_A^0}{C_A} \right). \quad (24) \]

Figure 5 with one modification (the intercept given by the last term of Eq. 24), shows how to test for the kinetic expression of Eq. 9 with this device.

So far we have illustrated how to use the batch, plug flow, and mixed flow reactors to search for the rate constants of a particular rate form, Eq. 9. The recycle reactor of Fig. 1d can also be used; however, except for high recycle rates where it approaches the behavior of a completely mixed reactor, its use offers no particular advantage.

As long as the deactivation is concentration independent any of the above experimental devices will give results which are simple to interpret. Thus all the above analyses can be extended with no difficulty to any order deactivation \( d \) and any order of reaction \( n \).

On the other hand if the deactivation is concentration dependent then the concentration and activity effects do not decouple and analysis becomes quite difficult unless the proper experimental device is used, one deliberately chosen so as to decouple these factors.

Let us consider this case next.

**Batch-Solids: Finding the Rate Equation when the Deactivation is Concentration Dependent**

To decouple the activity and concentration effects in the rate we must choose an
experimental device which allows the deactivation order to be studied without interference of concentration effects. The key then is to keep constant the concentration term in the \( \frac{da}{dt} \) equation of Eqs. 4, 5, and 6 while searching for the deactivation order. After this the concentration effect can be studied. As examples of the concentrations to be kept constant:

For parallel deactivation (Eq. 4) keep \( C_A \) constant;
For series deactivation (Eq. 5) keep \( C_R \) constant;
For side-by-side deactivation (Eq. 6) keep \( C_P \) constant;
For independent deactivation (Eq. 7) no concentration need be kept constant.

The completely mixed flow reactor with controlled and changing flow rate of feed can satisfy this requirement for all these kinetic forms.

**Deactivation order for parallel deactivation.** We illustrate the method of analysis with general \( n, n', d \)-order kinetics for parallel deactivation, or Eq. 4. At constant \( C_A \) Eq. 9 becomes

\[
-r'_A = (k' C_A^n) a = k' a, \tag{25}
\]

\[
-\frac{da}{dt} = (k'_d C_A^{n'}) a^d = k'_d a^d. \tag{26}
\]

So for the mixed flow reactor and the rate of Eq. 25 we obtain

\[
\frac{W}{F_{A_0}} = \frac{X_A}{-r'_A} = \frac{X_A}{k' a} = \frac{C_{A_0} - C_A}{k'_d a C_{A_0}},
\]

or

\[
\tau' = \frac{C_{A_0} - C_A}{k' a}. \tag{27}
\]

Next, integrating Eq. 26 for various orders of deactivation, and then replacing in Eq. 27 and rearranging gives \( \tau' \) as a function of \( t \) as follows:

For zero order deactivation

\[
\frac{1}{\tau'} = \frac{k'}{C_{A_0} - C_A} - \frac{k' k'_d}{C_{A_0} - C_A} t; \tag{28}
\]

For first order deactivation

\[
\ln \tau' = \ln \frac{C_{A_0} - C_A}{k'} + k'_d t; \tag{29}
\]

For second order deactivation

\[
\tau' = \frac{C_{A_0} - C_A}{k' d} + \frac{(C_{A_0} - C_A) k'_d}{k'} t; \tag{30}
\]

For third order deactivation

\[
\tau'^2 = \left( \frac{C_{A_0} - C_A}{k'} \right)^2 + \left( \frac{C_{A_0} - C_A}{k'} \right)^2 2k'_d t; \tag{31}
\]

For \( d \)th order deactivation

\[
(\tau')^{d-1} = C_1 + C_2 t. \tag{32}
\]

Figure 6 then shows how to test for \( d \)th order deactivation. If the data fall on a straight line the guessed mechanism is correct, and the slope and intercept gives the constants \( k' \) and \( k'_d \).

After the order of deactivation is found then the concentration and temperature dependencies can be determined in turn. The procedure for this is similar to that for nondeactivating catalytic systems, is well known, and needs no discussion here.

**Deactivation order for other types of deactivation.** The above development shows how to treat parallel deactivation. The analysis is quite similar for series deactivation if \( C_A \), hence \( C_R \) is kept constant, and for side-by-side deactivation if \( C_P \) and, if possible, \( C_A \) are kept constant. If \( C_A \) cannot be kept constant in side-by-side deactivation, analysis is still not particularly difficult.

**Flowing-solids Experimental Reactors**

Devices where the through flow of gas and solid, with flow patterns known, are
much more difficult to build and operate. They are only used when the simpler batch-solids system cannot be used, this means for reactions with very fast deactivation.

The fluidized bed reactor is probably the simplest of these devices, and under steady-state flow and with flow pattern known (this usually is the difficulty with this type of set up) integration and testing of some of the simpler rate forms is possible. Levenspiel (3) and Kunii and Levenspiel (4) show how to test rate equations with the following reaction and deactivation orders

\[ n = 1; \quad n' = 0.1; \quad d = 1.3 \]

either in a single reactor or in reactor-regenerator systems in which catalyst is continually recirculated between units.

Extension to other reaction and deactivation orders can be done. We need not consider this problem here.

**DISCUSSION**

This paper explores the usefulness to the experimenter of rate equations having \( n \)th order kinetics and decay (Eqs. 4–7). We ask in particular whether experiments can be devised so as to give simply the orders and rate constants of these equations.

1. We show that numerous experimental devices can be used to run experiments and to test kinetic forms where deactivation in concentration independent. These include reactors using either a batch or steady through flow of solids, and a batch, steady through flow or continually changing through flow of fluid.

2. To test the general rate form with concentration dependent deactivation the most useful reactor set up uses a batch of solids and mixed flow of fluid with changing flow rate so as to keep the concentration of the pertinent reaction component unchanged with time within the reactor. Thus by constantly lowering the flow rate in a basket or recycle reactor the activity and concentration dependencies can be decoupled and studied separately.

3. The rate equations treated here certainly do not cover all possible cases; however, they should suffice to show the generality of the method of analysis. Thus we conclude that the integral and differential methods of testing rate equations for homogeneous reactions can be extended without undue difficulty to systems of deactivating catalysts as long as the proper reactor type is selected for the experiment and as long as the rate is expressed in the form of Eqs. 4–7.

**REFERENCES**


