

R10.2 Analysis of Decay Laws

Determination of decay order for known reaction order,  $n$

**Integral Method** When the concentrations of reactants and products in the gas phase change very slowly with time, the pseudo-steady-state forms of the mole balances can be used. For the irreversible  $n$ th-order reaction carried out in a CSTR or in a differential reactor with catalyst weight  $W$ ,



the mole balance is

$$F_{A0} - F_A = -r'_A a(t) W \tag{R10-2.1}$$

Solving for the activity,  $a(t)$ , gives us

Using the pseudo-steady-state hypothesis

$$a(t) = \frac{v_0 C_{A0} - v_0 C_A}{W(-r'_A)} = \frac{v_0}{W} \left( \frac{C_{A0} - C_A}{k C_A^n} \right) \tag{R10-2.2}$$

where  $C_A$  is the effluent reactant concentration at time  $t$ .

In our efforts to determine the order of decay, we assume that the main reaction order is a known quantity. If it is not, a dual-model trial-and-error solution is necessary. *The idea is to find the simplest model that fits the data.* If we assume first-order decay,

$$a(t) = e^{-k_d t} = \frac{v_0}{Wk} \left( \frac{C_{A0} - C_A}{C_A} \right) \tag{R10-2.3}$$

Substituting in  $k_R = Wk/v_0$  and taking the log of both sides, we obtain

$$k_d t = \ln k_R + \ln \frac{C_A^n}{C_{A0} - C_A} \tag{R10-2.4}$$

The plot of  $\ln[C_A^n/(C_{A0} - C_A)]$  versus  $t$  should be a straight line whose slope is the deactivation rate constant (Figure R10-2.1). The specific reaction rate constant  $k$  can be calculated from the intercept.

First-order decay in a CSTR

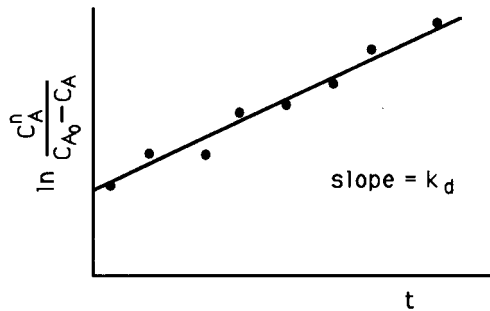


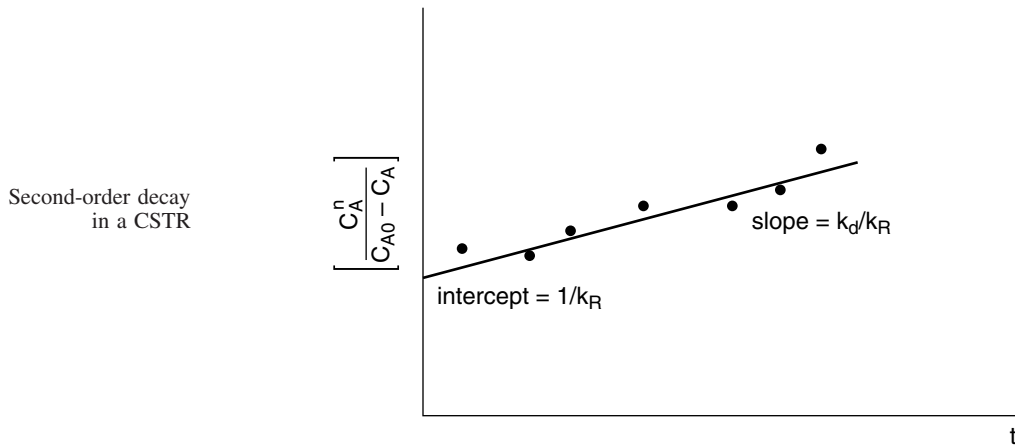
Figure R10-2.1 Integral method for first-order decay in a CSTR.

If first-order decay does not fit the data, one could try second-order decay:

$$= \frac{1}{1 + k_d t} = \frac{C_{A0} - C_A}{k_R C_A^n}$$

$$\boxed{\frac{C_A^n}{C_{A0} - C_A} = \frac{1}{k_R} + \frac{k_d}{k_R} t} \quad (\text{R10-2.5})$$

Consequently, both  $k_R$  and  $k_d$  can be found from a plot of  $[C_A^n / (C_{A0} - C_A)]$  versus  $t$ , as shown in Figure R10-2.2. We can continue assuming decay orders in this manner until the decay rate law is found.



**Figure R10-2.2** Integral method for second-order decay in a CSTR.

For a packed-bed reactor, the approach is quite similar to that described for a CSTR. For a first-order reaction, the combined mole balance and rate law is

$$v_0 \frac{dC_A}{dW} = -ka(t) C_A \quad (\text{R10-2.6})$$

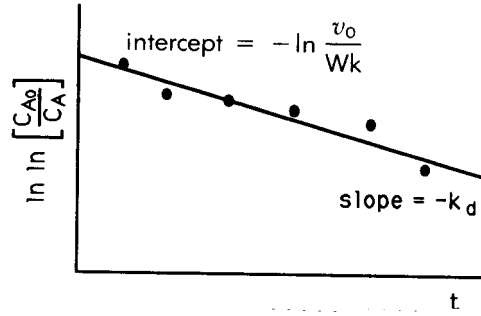
Solving for  $a(t)$  for the case of uniform activity throughout the reactor yields

$$a(t) = \frac{v_0}{Wk} \ln \frac{C_{A0}}{C_A} \quad (\text{R10-2.7})$$

For first-order decay,  $a = e^{-k_d t}$  (see Figure R10-2.3), we take the log of both sides:

$$\boxed{-k_d t = \ln \frac{v_0}{Wk} + \ln \ln \frac{C_{A0}}{C_A}} \quad (\text{R10-2.8})$$

First-order decay,  
first-order reaction  
in a packed bed



**Figure R10-2.3** Integral method for first-order decay in a packed-bed reactor.

If the concentration–time data do not fit the deactivation law, another decay law is chosen and the process is repeated.

The general idea of the three previous cases (i.e., Figures R10-2.1 through R10-2.3) is to arrange the data in such a fashion as to arrive at functional groupings of measured variables that will be linear with time. The particular functional groups will vary with (1) type of reactor used to collect the data, (2) reaction order of the main reaction, and (3) the decay reaction order. For the three main types of reactors, three main reaction rate laws, and three decay rates, *27 different types of plots could result*. We leave derivation of the equation for each of these plots to the reader and point out that only one additional step is needed in our solution algorithm. That step is the decay rate law:

The type of plot used to find  $k_d$  and  $k_R$  depends upon

- Type of reactor
- Decay law
- Rate law

Once again:  
the algorithm

