# Elements of Chemical Reaction Engineering

## Sixth Edition

H. Scott Fogler

# Elements of Chemical Reaction Engineering

*Sixth Edition*

### 7.5.2  Model Discrimination

One can also determine which model or equation best fits the experimental data by comparing the sums of the squares for each model and then choosing the equation with a smaller sum of squares and/or carrying out an F-test. Alternatively, we can compare the residual plots for each model. These plots show the error associated with each data point, and one looks to see whether the error is randomly distributed or whether there is a trend in the error. When the error is randomly distributed, this is an additional indication that the correct rate law has been chosen. An example of model discrimination using nonlinear regression is given in Chapter 10, Example 10-3.

## 7.6  Reaction-Rate Data from Differential Reactors

Data acquisition using the method of initial rates and a differential reactor is similar in that the rate of reaction is determined for a specified number of predetermined initial or entering reactant concentrations. A differential reactor (PBR) is normally used to determine the rate of reaction as a function of either concentration or partial pressure. It consists of a tube containing a very small amount of catalyst, usually arranged in the form of a thin wafer or disk. A typical arrangement is shown schematically in Figure 7-8. The criterion for a reactor being differential is that the conversion of the reactants in the bed is extremely small, as is the change in temperature and reactant concentration through the bed. As a result, the reactant concentration through the reactor is essentially constant and approximately equal to the inlet concentration. That is, the reactor is considered to be gradientless,[4] and the reaction rate is considered spatially uniform within the bed.

> *Most commonly used catalytic reactor to obtain experimental data*

The differential reactor is relatively easy to construct at a low cost. Owing to the low conversion achieved in this reactor, the heat release per unit volume will be small (or can be made small by diluting the bed with inert solids) so that the reactor operates essentially in an isothermal manner. When operating this reactor, precautions must be taken so that the reactant gas or liquid does not bypass or channel through the packed catalyst, but instead flows uniformly across the catalyst. If the catalyst under investigation decays rapidly, as discussed in Chapter 10, the differential reactor is not a good choice because the reaction-rate parameters at the start of a run will be different from those at the end of the run. In some cases, sampling and analysis of the product stream may be difficult for small conversions in multicomponent systems.

> *Limitations of the differential reactor*

> *The differential reactor is operated at steady state.*
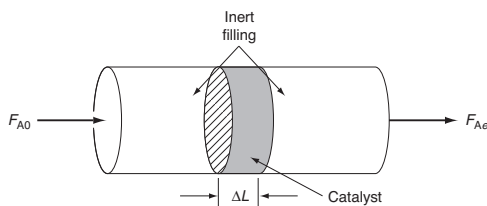


**Figure 7-8**  Differential reactor.
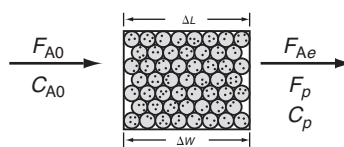


**Figure 7-9**  Differential catalyst bed.

---

[4] B. Anderson, ed., *Experimental Methods in Catalytic Research,* San Diego, CA: Academic Press.

For the reaction of species A going to product (P)

$$A \rightarrow P$$

the volumetric flow rate through the catalyst bed is monitored, as are the entering and exiting concentrations (Figure 7-9). Therefore, if the weight of catalyst, $\Delta W$, is known, the rate of reaction per unit mass of catalyst, $-r'_A$, can be calculated. Since the differential reactor is assumed to be *gradientless*, the design equation will be similar to the CSTR design equation. A steady-state mole balance on reactant A gives

$$\begin{bmatrix} \text{Flow} \\ \text{rate} \\ \text{in} \end{bmatrix} - \begin{bmatrix} \text{Flow} \\ \text{rate} \\ \text{out} \end{bmatrix} + \begin{bmatrix} \text{Rate of} \\ \text{generation} \end{bmatrix} = \begin{bmatrix} \text{Rate of} \\ \text{accumulation} \end{bmatrix}$$

$$[F_{A0}] - [F_{Ae}] + \left[ \left( \frac{\text{Rate of reaction}}{\text{Mass of catalyst}} \right)(\text{Mass of catalyst}) \right] = 0$$

$$F_{A0} - F_{Ae} + (r'_A)(\Delta W) = 0$$

The subscript $e$ refers to the *exit* of the reactor. Solving for $-r'_A$, we have

$$-r'_A = \frac{F_{A0} - F_{Ae}}{\Delta W} \tag{7-26}$$

The mole balance equation can also be written in terms of concentration

$$\boxed{-r'_A = \frac{v_0 C_{A0} - v C_{Ae}}{\Delta W}} \tag{7-27}$$

or in terms of conversion or product flow rate $F_P$

$$\boxed{-r'_A = \frac{F_{A0} X}{\Delta W} = \frac{F_P}{\Delta W}} \tag{7-28}$$

The term $F_{A0} X$ gives the rate of formation of product, $F_P$, when the stoichiometric coefficients of A and of P are identical. Adjustments to Equation (7-28) must be made when this is not the case.

For constant volumetric flow, Equation (7-28) reduces to

$$-r'_A = \frac{v_0 (C_{A0} - C_{Ae})}{\Delta W} = \frac{v_0 C_P}{\Delta W} \tag{7-29}$$

Consequently, we see that the reaction rate, $-r'_A$, can be determined by measuring the product concentration, $C_P$.

By using very little catalyst and large volumetric flow rates, the concentration difference, $(C_{A0} - C_{Ae})$, can be made quite small. The rate of reaction determined from Equation (7-29) can be obtained as a *function* of the reactant concentration in the catalyst bed, $C_{Ab}$

$$-r'_A = -r'_A(C_{Ab}) \tag{7-30}$$

by varying the inlet concentration. One approximation of the concentration of A within the bed, $C_{Ab}$, would be the arithmetic mean of the inlet and outlet concentrations

$$C_{Ab} = \frac{C_{A0} + C_{Ae}}{2} \tag{7-31}$$

However, since very little reaction takes place within the bed, the bed concentration is essentially equal to the inlet concentration

$$C_{Ab} \approx C_{A0}$$

so $-r'_A$ is a function of $C_{A0}$

$$-r'_A = -r'_A(C_{A0}) \tag{7-32}$$

**CAUTION**

As with the method of initial rates (see the CRE Web site, *http://www.umich.edu/~elements/6e/software/nonlinear_regression_tutorial.pdf*), we find $-r_{A0}$ as a function of $C_{A0}$ and then use various numerical and graphical techniques to determine the appropriate algebraic equation for the rate law. When collecting data for fluid–solid reacting systems, care must be taken that we use high flow rates through the differential reactor and small catalyst particle sizes in order to avoid mass transfer–limitations. If data show the reaction to be first order with a low activation energy, say 8 kcal/mol, one should suspect the data are being collected in the mass transfer–limited regime. We will expand on mass transfer–limitations and how to avoid them in Chapter 10, and also in Chapters 14 and 15.

---

***Example 7–4    Using a Differential Reactor to Obtain Catalytic Rate Data***

The formation of methane from carbon monoxide and hydrogen using a nickel catalyst was studied by Pursley.[5] The reaction

$$3H_2 + CO \rightarrow CH_4 + H_2O$$
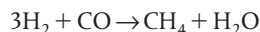
was carried out at 500°F in a differential reactor where the effluent concentration of methane was measured. The raw data is shown in Table E7-4.1.

TABLE E7-4.1    RAW DATA

| Run | $P_{CO}$ (atm) | $P_{H_2}$ (atm) | $C_{CH_4}$ (mol/dm³) |
|-----|----------------|-----------------|----------------------|
| 1   | 1              | 1.0             | $1.73 \times 10^{-4}$ |
| 2   | 1.8            | 1.0             | $4.40 \times 10^{-4}$ |
| 3   | 4.08           | 1.0             | $10.0 \times 10^{-4}$ |
| 4   | 1.0            | 0.1             | $1.65 \times 10^{-4}$ |
| 5   | 1.0            | 0.5             | $2.47 \times 10^{-4}$ |
| 6   | 1.0            | 4.0             | $1.75 \times 10^{-4}$ |

$P_{H_2}$ is constant in Runs 1, 2, 3. $P_{CO}$ is constant in Runs 4, 5, 6.

---

[5] J. A. Pursley, "An investigation of the reaction between carbon monoxide and hydrogen on a nickel catalyst above one atmosphere," Ph.D. thesis, University of Michigan.

The exit volumetric flow rate from a differential packed bed containing 10 g of catalyst was maintained at $S_0 = 300$ dm³/min for each run. The partial pressures of $H_2$ and CO were determined at the entrance to the reactor, and the methane concentration was measured at the reactor exit.

Determine the rate law and rate-law parameters. To better understand how we will determine the rate law and its parameters, we will break the solution into three parts, **(a)**, **(b)**, and **(c)**, as shown below.

(a) ***Relate the rate of reaction to the exit methane concentration.*** The reaction-rate law is assumed to be the product of a function of the partial pressure of CO, $f(CO)$, and a function of the partial pressure of $H_2$, $g(H_2)$, that is,

$$r'_{CH_4} = f(CO) \cdot g(H_2) \qquad \text{(E7-4.1)}$$

(b) ***Determine the rate-law dependence on carbon monoxide,*** using the data generated in part **(a)**. Assume that the functional dependence of $r'_{CH_4}$ on $P_{CO}$ is of the form

$$r'_{CH_4} \sim P_{CO}^\alpha \qquad \text{(E7-4.2)}$$

(c) ***Generate a table of the reaction rate as a function of partial pressures*** of carbon monoxide and hydrogen, and then determine the rate-law dependence on $H_2$.

*Solution*

**(a) Calculate the Rates of Reaction.** In this example the product composition, rather than the reactant concentration, is being monitored. The term $(-r'_{CO})$ can be written in terms of the flow rate of methane from the reaction

$$-r'_{CO} = r'_{CH_4} = \frac{F_{CH_4}}{\Delta W}$$

Substituting for $F_{CH_4}$ in terms of the volumetric flow rate and the concentration of methane gives

$$\boxed{r'_{CH_4} = \frac{v_0 C_{CH_4}}{\Delta W}} \qquad \text{(E7-4.3)}$$

Since $v_0$, $C_{CH_4}$, and $\Delta W$ are known for each run, we can calculate the rate of reaction.

For run 1

$$r'_{CH_4} = \left(\frac{300 \text{ dm}^3}{\text{min}}\right) \frac{1.73 \times 10^{-4}}{10 \text{ g-cat}} \text{ mol/dm}^3 = 5.2 \times 10^{-3} \frac{\text{mol CH}_4}{\text{g-cat} \times \text{min}}$$

The rate for runs 2 through 6 can be calculated in a similar manner (Table E7-4.2).

TABLE E7-4.2    RAW AND CALCULATED DATA

| Run | $P_{CO}$ (atm) | $P_{H_2}$ (atm) | $C_{CH_4}$ (mol/dm³) | $r'_{CH_4} \left(\dfrac{\text{mol CH}_4}{\text{g-cat} \cdot \text{min}}\right)$ |
|---|---|---|---|---|
| 1 | 1.0 | 1.0 | $1.73 \times 10^{-4}$ | $5.2 \times 10^{-3}$ |
| 2 | 1.8 | 1.0 | $4.40 \times 10^{-4}$ | $13.2 \times 10^{-3}$ |
| 3 | 4.08 | 1.0 | $10.0 \times 10^{-4}$ | $30.0 \times 10^{-3}$ |
| 4 | 1.0 | 0.1 | $1.65 \times 10^{-4}$ | $4.95 \times 10^{-3}$ |
| 5 | 1.0 | 0.5 | $2.47 \times 10^{-4}$ | $7.42 \times 10^{-3}$ |
| 6 | 1.0 | 4.0 | $1.75 \times 10^{-4}$ | $5.25 \times 10^{-3}$ |

**(b) Determining the Rate-Law Dependence in CO.** For constant hydrogen concentration (runs 1, 2, and 3), the rate law

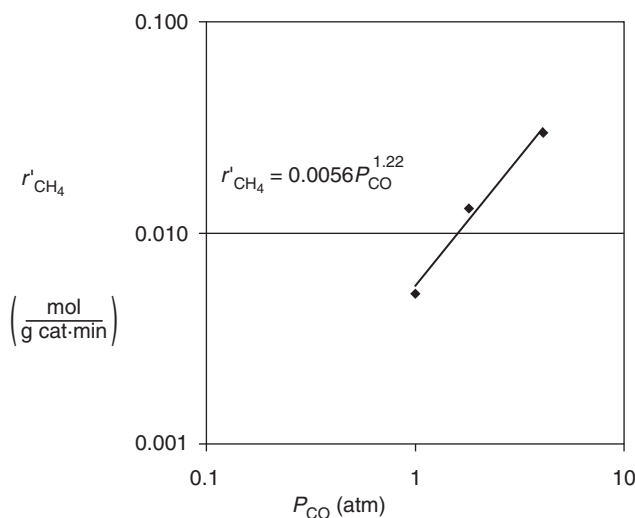$$r'_{CH_4} = \overbrace{k\,g(P_{H_2})}^{k'}\,P_{CO}^{\alpha}$$

can be written as

$$r'_{CH_4} = k'P_{CO}^{\alpha} \qquad\qquad (E7\text{-}4.4)$$

Taking the natural log of Equation (E7-4.4) gives us

$$\ln(r'_{CH_4}) = \ln k' + \alpha \ln P_{CO}$$

We now plot $\ln(r'_{CH_4})$ versus $\ln P_{CO}$ using runs 1, 2, and 3, for which the $H_2$ concentration is constant, in Figure E7-4.1. We see from the Excel plot that $\alpha = 1.22$.



**Figure E7-4.1**    Reaction rate as a function of concentration.

If we had used more data (not given here) we would have found $\alpha = 1$.

Had we not been so pressed for time and included more points, we would have found that the reaction is essentially first order with $\alpha = 1$, that is

$$-r'_{CO} = k'P_{CO} \qquad\qquad (E7\text{-}4.5)$$

From the first three data points in Table E7-4.2 where the partial pressure of $H_2$ is constant, we see the rate is linear in partial pressure of CO

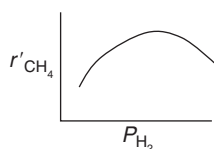$$r'_{CH_4} = k\,P_{CO}\cdot g(H_2)$$

Now let's look at the hydrogen dependence.

**(c) Determining the Rate-Law Dependence on $H_2$.** It will not be intuitively obvious how to do this analysis until you have studied Chapter 10 where we have rate laws with concentrations or partial pressures in both the numerator **and** denominator of the rate law. From Table E7-4.2 it appears that the dependence of $r'_{CH_4}$ on $P_{H_2}$ cannot be represented by a power law. Comparing run 4 with run 5 and then run 5 with run 6, we see that the reaction rate first increases with increasing partial pressure of hydrogen, and subsequently decreases with increasing $P_{H_2}$. That is, there

appears to be a concentration of hydrogen at which the rate is maximum. One set of rate laws that is consistent with these observations is:

1. At low $H_2$ concentrations where $r'_{CH_4}$ increases as $P_{H_2}$ increases, the rate law may be of the form

$$r'_{CH_4} \sim P_{H_2}^{\beta_1} \tag{E7-4.6}$$

2. At high $H_2$ concentrations where $r'_{CH_4}$ decreases as $P_{H_2}$ increases, the rate law may be of the form

$$r'_{CH_4} \sim \frac{1}{P_{H_2}^{\beta_2}} \tag{E7-4.7}$$

We would like to find one rate law that is consistent with reaction-rate data at both high and low hydrogen concentrations. After we have studied heterogeneous reactions in Chapter 10, we would recognize that Equations (E7-4.6) and (E7-4.7) can be combined into the form

$$r'_{CH_4} \sim \frac{P_{H_2}^{\beta_1}}{1 + bP_{H_2}^{\beta_2}} \tag{E7-4.8}$$

We will see in Chapter 10 that this combination and similar rate laws that have reactant concentrations (or partial pressures) in the numerator and denominator are common in *heterogeneous catalysis*.

Let's see if the resulting rate law (E7-4.8) is qualitatively consistent with the rate observed.

1. *For condition 1*: At low $P_{H_2}$, $[b(P_{H_2})^{\beta_2} \ll 1]$ and Equation (E7-4.8) reduces to

$$r'_{CH_4} \sim P_{H_2}^{\beta_1} \tag{E7-4.9}$$

Equation (E7-4.9) is consistent with the trend in comparing runs 4 and 5.

2. *For condition 2*: At high $P_{H_2}$, $[b(P_{H_2})^{\beta_2} \gg 1]$ and Equation (E7-4.8) reduces to

$$r'_{CH_4} \sim \frac{(P_{H_2})^{\beta_1}}{(P_{H_2})^{\beta_2}} \sim \frac{1}{(P_{H_2})^{\beta_2 - \beta_1}} \tag{E7-4.10}$$

where $\beta_2 > \beta_1$. Equation (E7-4.10) is consistent with the trends in comparing runs 5 and 6.

Combining Equations (E7-4.8) and (E7-4.5)

Typical form of the rate law for heterogeneous catalysis

$$r'_{CH_4} = \frac{aP_{CO}P_{H_2}^{\beta_1}}{1 + bP_{H_2}^{\beta_2}} \tag{E7-4.11}$$

We now use the Polymath regression program to find the parameter values $a$, $b$, $\beta_1$, and $\beta_2$. The results are shown in Table E7-4.3.

The corresponding rate law is

$$r'_{CH_4} = \frac{0.025P_{CO}P_{H_2}^{0.61}}{1 + 2.49P_{H_2}} \tag{E7-4.12}$$

Sketch of $r'_{CH_4}$ as a function of $P_{H_2}$



$r'_{CH_4}$

$P_{H_2}$