R5.1 Least-Squares Analysis

R5.1.1 Linearization of the Rate Law

If a rate law depends on the concentration of more than one species and it is not possible to use the method of excess, we may choose to use a linearized least-squares method. This method of data analysis is also useful to determine the best values of the rate law parameters from a series of measurements when three or more parameters are involved (e.g., reaction order, α; frequency factor, *A*; and activation energy, *E*).

A mole balance on a constant-volume batch reactor gives

$$-\frac{dC_A}{dt} = -r_A = kC_A^\alpha C_B^\beta \tag{R5-1}$$

If we now use the method of initial rates, then

$$\left(-\frac{dC_A}{dt}\right)_0 = -r_{A0} = kC_{A0}^\alpha C_{B0}^\beta$$

Taking the log of both sides, we have

Used when C_{A0} and C_{B0} are varied simultaneously

$$\boxed{\ln\left(-\frac{dC_A}{dt}\right)_0 = \ln k + \alpha \ln C_{A0} + \beta \ln C_{B0}} \tag{R5-2}$$

Let $Y = \ln(-dC_A/dt)_0$, $X_1 = \ln C_{A0}$, $X_2 = \ln C_{B0}$, $a_0 = \ln k$, $a_1 = \alpha$, and $a_2 = \beta$. Then

$$Y = a_0 + a_1X_1 + a_2X_2 \tag{R5-3}$$

If we now carry out *N* experimental runs, for the *j*th run, Equation (R5-3) takes the form

$$\boxed{Y_j = a_0 + a_1X_{1j} + a_2X_{2j}} \tag{R5-4}$$

where $X_{1j} = \ln C_{A0j}$, with C_{A0j} being the initial concentration of A for the *j*th run. The best values of the parameters a_0, a_1, and a_2 are found by solving Equations (R5-5) through (R5-7) simultaneously.

For *N* runs, 1, 2, …, *N*,

$$\sum_{j=1}^{N} Y_j = Na_0 + a_1\sum_{j=1}^{N} X_{1j} + a_2\sum_{j=1}^{N} X_{2j} \tag{R5-5}$$

Three equations, three unknowns (a_0, a_1, a_2)

$$\sum_{j=1}^{N} X_{1j}Y_j = a_0\sum_{j=1}^{N} X_{1j} + a_1\sum_{j=1}^{N} X_{1j}^2 + a_2\sum_{j=1}^{N} X_{1j}X_{2j} \tag{R5-6}$$

$$\sum_{j=1}^{N} X_{2j}Y_j = a_0\sum_{j=1}^{N} X_{2j} + a_1\sum_{j=1}^{N} X_{1j}X_{2j} + a_2\sum_{j=1}^{N} X_{2j}^2 \qquad \text{(R5-7)}$$

We have three linear equations and three unknowns which we can solve for: a_0, a_1, and a_2. A detailed example delineating the kinetics of the reaction

$$H_2(g) + C_8H_{16}(g) \rightarrow C_8H_{18}(g)$$

using linear least-squares analysis can be found in Example 10-2. If we set $a_2 = 0$ and consider only two variables, Y and X, Equations (R5-5) and (R5-6) reduce to the familiar least-squares equations for two unknowns.

Example R5–5 Using Least-Squares Analysis to Determine Rate Law Parameters

A 10^5 fold increase in reaction rate!!!

The etching of semiconductors in the manufacture of computer chips is another important solid–liquid dissolution reaction (see Problem P5-12 and Section 12.10). The dissolution of the semiconductor MnO_2 was studied using a number of different acids and salts. The rate of dissolution was found to be a function of the reacting liquid solution redox potential relative to the energy-level conduction band of the semiconductor. It was found that the reaction rate could be increased by a factor of 10^5 simply by changing the anion of the acid[1]!! From the following data, determine the reaction order and specific reaction rate for the dissolution of MnO_2 in HBr.

C_{A0} (mol HBr/dm^3)	0.1	0.5	1.0	2.0	4.0
$-r''_{A0}$ (mol HBr/m$^2\cdot$h) $\times 10^2$	0.073	0.70	1.84	4.86	12.84

Solution

We assume a rate law of the form

$$-r''_{HBr} = kC_{HBr}^{\alpha} \qquad \text{(RE5-5.1)}$$

Letting A = HBr, taking the ln of both sides of (RE5-5.1), and using the initial rate and concentration gives

$$\ln(-r''_{A0}) = \ln k + \alpha \ln C_{A0} \qquad \text{(RE5-5.2)}$$

Let $Y = \ln(-r''_{A0})$, $a = \ln k$, $b = \alpha$, and $X = \ln C_{A0}$. Then

$$Y = a + bX \qquad \text{(RE5-5.3)}$$

The least-squares equations to be solved for the best values of a and b are for N runs

$$\sum_{i=1}^{N} Y_i = Na + b\sum_{i=1}^{N} X_i \qquad \text{(RE5-5.4)}$$

$$\sum_{i=1}^{N} X_iY_i = a\sum_{i=1}^{N} X_i + b\sum_{i=1}^{N} X_i^2 \qquad \text{(RE5-5.5)}$$

[1] S. E. Le Blanc and H. S. Fogler, *AIChE J., 32*, 1702 (1986).

where i = run number. Substituting the appropriate values from Table RE5-5.1 into Equations (RE5-5.4) and (RE5-5.5) gives

$$-21.26 = 5a + -0.92b \tag{RE5-5.6}$$

$$15.10 = -0.92a + 8.15b \tag{RE5-5.7}$$

TABLE RE5-5.1

Run	C_{A0}	X_i	$-r''_{A0}$	Y_i	X_iY_i	X_i^2
1	0.1	−2.302	0.00073	−7.22	16.61	5.29
2	0.5	−0.693	0.007	−4.96	3.42	0.48
3	1.0	0.0	0.0184	−4.0	0.0	0.0
4	2.0	0.693	0.0486	−3.02	−2.09	0.48
5	4.0	1.38	0.128	−2.06	−2.84	1.90
		$\sum_{i=1}^{5} X_i = -0.92$		$\sum_{i=1}^{5} Y_i = -21.26$	$\sum_{i=1}^{5} X_iY_i = 15.1$	$\sum_{i=1}^{5} X_i^2 = 8.15$

Solving for a and b yields

$$b = 1.4 \quad \text{therefore} \quad \alpha = 1.4$$

and

$$a = -3.99 \qquad k = 1.84 \times 10^{-2}\,(\text{dm}^3/\text{mol})^{0.4}/\text{m}^2 \cdot \text{h}$$

$$\boxed{r''_{HBr} = 0.0184 C_{HBr}^{1.4}} \tag{RE5-5.8}$$