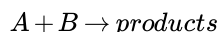


9.2: The Method of Initial Rates

The **method of initial rates** is a commonly used technique for deriving rate laws. As the name implies, the method involves measuring the initial rate of a reaction. The measurement is repeated for several sets of initial concentration conditions to see how the reaction rate varies. This might be accomplished by determining the time needed to exhaust a particular amount of a reactant (preferably one on which the reaction rate does not depend!) A typical set of data for a reaction



might appear as follows:

Run	[A] (M)	[B] (M)	Rate (M/s)
1	0.0100	0.0100	0.0347
2	0.0200	0.0100	0.0694
3	0.0200	0.0200	0.2776

The analysis of this data involves taking the ratios of rates measured where one of the concentrations does not change. For example, assuming a rate law of the form

$$\text{rate} = k[A]^\alpha [B]^\beta \quad (9.2.1)$$

The ratio of runs i and j generate the following relationship.

$$\frac{\text{rate}_i}{\text{rate}_j} = \frac{k[A]_i^\alpha [B]_i^\beta}{k[A]_j^\alpha [B]_j^\beta}$$

So using runs 1 and 2,

$$\frac{0.0347 \text{ M/s}}{0.0694 \text{ M/s}} = \frac{\cancel{k}(0.01 \text{ M/s})^\alpha \cancel{(0.01 \text{ M/s})}^\beta}{\cancel{k}(0.02 \text{ M/s})^\alpha \cancel{(0.01 \text{ M/s})}^\beta}$$

this simplifies to

$$\frac{1}{2} = \left(\frac{1}{2}\right)^\alpha$$

So clearly, $\alpha = 1$ and the reaction is 1st order in A. Taking the ratio using runs 2 and 3 yields

$$\frac{0.0694 \text{ M/s}}{0.2776 \text{ M/s}} = \frac{\cancel{k}(0.02 \text{ M})^\alpha \cancel{(0.01 \text{ M})}^\beta}{\cancel{k}(0.02 \text{ M})^\alpha \cancel{(0.02 \text{ M})}^\beta}$$

This simplifies to

$$\frac{1}{4} = \left(\frac{1}{2}\right)^\beta \quad (9.2.2)$$

By inspection, one can conclude that $\beta = 2$, and that the reaction is second order in B. But if it is not so clear (as it might not be if the concentration is not incremented by a factor of 2), the value of β can be determined by taking the natural logarithm of both sides of the Equation 9.2.2.

$$\begin{aligned} \ln \frac{1}{4} &= \ln \left(\frac{1}{2}\right)^\beta \\ &= \beta \ln \left(\frac{1}{2}\right) \end{aligned}$$

dividing both sides by $\ln(1/2)$

$$\frac{\ln\left(\frac{1}{4}\right)}{\ln\left(\frac{1}{2}\right)} = \beta \frac{\ln\left(\frac{1}{2}\right)}{\ln\left(\frac{1}{2}\right)}$$

or

$$\beta = \frac{-1.3863}{-0.69315} = 2$$

And so the rate law (Equation 9.2.1) can be expressed as

$$\text{rate} = k[A][B]^2$$

And is 1st order in A, 2nd order in B, and 3rd order overall. The rate constant can then be evaluated by substituting one of the runs into the rate law (or using all of the data and taking an average). Arbitrarily selecting the first run for this,

$$0.0347 \text{ M/s} = k(0.01 \text{ M/s})(0.01 \text{ M/s})^2$$

This results in a value of k

$$k = \frac{0.0347 \text{ M/s}}{(0.01 \text{ M/s})(0.01 \text{ M/s})^2} = 3.47 \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$$

It is useful to note that the units on k are consistent with a 3rd order rate law.

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