Rate Law Determination - Method of Initial Rates

Example #1

Overall equation: $1H_2(g) + 1I_2(g) \longrightarrow 2HI(g)$

Expt. #	$[H_2]_o$	$[I_2]_o$	Measured initial rate
1	0.0113M	0.0011M	1.9×10^{-23} M/sec
2	0.0220M	0.0033M	1.1×10^{-22} M/sec
3	0.0550M	0.0011M	9.3×10^{-23} M/sec
4	0.0220M	0.0056M	1.9×10^{-22} M/sec

Determine: $\text{rate} = k[H_2]^x[I_2]^y$

Find the numerical value of the specfic rate constant, k.

Rate Law Determination - Method of Initial Rates

Example #1

Overall equation: $1H_2(g) + 1I_2(g) \longrightarrow 2HI(g)$

Expt. #	$[H_2]_o$	$[I_2]_o$	Measured initial rate
1	0.0113M	0.0011M	1.9×10^{-23} M/sec
2	0.0220M	0.0033M	1.1×10^{-22} M/sec
3	0.0550M	0.0011M	9.3×10^{-23} M/sec
4	0.0220M	0.0056M	1.9×10^{-22} M/sec

Determine: $\text{rate} = k[H_2]^x[I_2]^y$

Find the numerical value of the specfic rate constant, k.

Solve for x using data from experiments #3 &#1:

$$\left(\frac{0.0550M}{0.0113M}\right)^x = \frac{9.3 \times 10^{-23}\ \text{M/sec}}{1.9 \times 10^{-23}\ \text{M/sec}} \qquad (4.87)^x = 4.89 \qquad x = 1$$

Rate Law Determination - Method of Initial Rates

Example #1

Overall equation: $1H_2\,(g) + 1I_2\,(g) \longrightarrow 2HI(g)$

Expt. #	$[H_2]_o$	$[I_2]_o$	Measured initial rate
1	0.0113M	0.0011M	$1.9\text{x}10^{-23}$ M/sec
2	0.0220M	0.0033M	$1.1\text{x}10^{-22}$ M/sec
3	0.0550M	0.0011M	$9.3\text{x}10^{-23}$ M/sec
4	0.0220M	0.0056M	$1.9\text{x}10^{-22}$ M/sec

Determine: $\text{rate} = k[H_2]^x[I_2]^y$

Find the numerical value of the specfic rate constant, k.

Solve for x using data from experiments #3 &#1:

$$\left(\frac{0.0550M}{0.0113M}\right)^x = \frac{9.3\text{x}10^{-23}\ \text{M/sec}}{1.9\text{x}10^{-23}\ \text{M/sec}} \qquad (4.87)^x = 4.89 \qquad x = 1$$

Solve for y using data from experiments #4 &#2:

$$\left(\frac{0.0056M}{0.0033M}\right)^y = \frac{1.9\text{x}10^{-22}\ \text{M/sec}}{1.1\text{x}10^{-22}\ \text{M/sec}} \qquad (1.70)^y = 1.73 \qquad y = 1$$

$$\text{rate} = k[H_2]^1[I_2]^1$$

Rate Law Determination - Method of Initial Rates

Example #1

Overall equation: $1H_2(g) + 1I_2(g) \longrightarrow 2HI(g)$

Expt. #	$[H_2]_o$	$[I_2]_o$	Measured initial rate
1	0.0113M	0.0011M	$1.9\text{x}10^{-23}$ M/sec
2	0.0220M	0.0033M	$1.1\text{x}10^{-22}$ M/sec
3	0.0550M	0.0011M	$9.3\text{x}10^{-23}$ M/sec
4	0.0220M	0.0056M	$1.9\text{x}10^{-22}$ M/sec

$$\text{rate} = k[H_2]^1[I_2]^1$$

To solve for the numerical value of k, use the data from any one of the experiments:

From Expt. #1: $1.9\text{x}10^{-23}\text{ M/sec} = k(0.0113\text{M})^1(0.0011\text{M})^1$

$$k = \frac{1.9\text{x}10^{-23}\text{ M/sec}}{(0.0113\text{M})^1(0.0011\text{M})^1} = 1.53\text{x}10^{-18}\,(\text{M}\cdot\text{sec})^{-1}$$

Rate Law Determination - Method of Initial Rates

Example #2

Overall equation: $1\,BrO_3^{-1}(aq) + 5\,Br^{-1}(aq) + 6\,H^{+1}(aq) \longrightarrow 3\,Br_2(liq) + 3\,H_2O(liq)$

Expt. #	$[BrO_3^{-1}]_o$	$[Br^{-1}]_o$	$[H^{+1}]_o$	Measured initial rate
1	0.10M	0.10M	0.10M	8.0×10^{-4} M/sec
2	0.20M	0.10M	0.10M	1.6×10^{-3} M/sec
3	0.20M	0.20M	0.10M	3.2×10^{-3} M/sec
4	0.10M	0.10M	0.20M	3.2×10^{-3} M/sec

Determine: $\text{rate} = k[BrO_3^{-1}]^a[Br^{-1}]^b[H^{+1}]^c$

Find the numerical value of the specfic rate constant, k.

Rate Law Determination - Method of Initial Rates

Example #2

Overall equation: $1\,BrO_3^{-1}(aq) + 5\,Br^{-1}(aq) + 6\,H^{+1}(aq) \longrightarrow 3\,Br_2(liq) + 3\,H_2O(liq)$

Expt. #	$[BrO_3^{-1}]_o$	$[Br^{-1}]_o$	$[H^{+1}]_o$	Measured initial rate
1	0.10M	0.10M	0.10M	$8.0x10^{-4}$ M/sec
2	0.20M	0.10M	0.10M	$1.6x10^{-3}$ M/sec
3	0.20M	0.20M	0.10M	$3.2x10^{-3}$ M/sec
4	0.10M	0.10M	0.20M	$3.2x10^{-3}$ M/sec

Determine: $\text{rate} = k[BrO_3^{-1}]^a[Br^{-1}]^b[H^{+1}]^c$

Find the numerical value of the specfic rate constant, k.

Solve for a using data from experiments #2 &#1:

$$\left(\frac{0.20M}{0.10M}\right)^a = \frac{1.6x10^{-3}\,M/sec}{8.0x10^{-4}\,M/sec} \qquad (2.0)^a = 2.0 \qquad a = 1$$

Rate Law Determination - Method of Initial Rates

Example #2

Overall equation: $1\,BrO_3^{-1}(aq) + 5\,Br^{-1}(aq) + 6\,H^{+1}(aq) \longrightarrow 3\,Br_2(liq) + 3\,H_2O(liq)$

Expt. #	$[BrO_3^{-1}]_o$	$[Br^{-1}]_o$	$[H^{+1}]_o$	Measured initial rate
1	0.10M	0.10M	0.10M	8.0×10^{-4} M/sec
2	0.20M	0.10M	0.10M	1.6×10^{-3} M/sec
3	0.20M	0.20M	0.10M	3.2×10^{-3} M/sec
4	0.10M	0.10M	0.20M	3.2×10^{-3} M/sec

Determine: $\text{rate} = k[BrO_3^{-1}]^a[Br^{-1}]^b[H^{+1}]^c$

Find the numerical value of the specfic rate constant, k.

Solve for a using data from experiments #2 &#1:

$$\left(\frac{0.20M}{0.10M}\right)^a = \frac{1.6\times10^{-3}\ M/sec}{8.0\times10^{-4}\ M/sec} \qquad (2.0)^a = 2.0 \qquad a = 1$$

Solve for b using data from experiments #3 &#2:

$$\left(\frac{0.20M}{0.10M}\right)^b = \frac{3.2\times10^{-3}\ M/sec}{1.6\times10^{-3}\ M/sec} \qquad (2.0)^b = 2.0 \qquad b = 1$$

Rate Law Determination - Method of Initial Rates

Example #2

Overall equation: $1\,BrO_3^{-1}(aq) + 5\,Br^{-1}(aq) + 6\,H^{+1}(aq) \longrightarrow 3\,Br_2(liq) + 3\,H_2O(liq)$

Expt. #	$[BrO_3^{-1}]_o$	$[Br^{-1}]_o$	$[H^{+1}]_o$	Measured initial rate
1	0.10M	0.10M	0.10M	8.0×10^{-4} M/sec
2	0.20M	0.10M	0.10M	1.6×10^{-3} M/sec
3	0.20M	0.20M	0.10M	3.2×10^{-3} M/sec
4	0.10M	0.10M	0.20M	3.2×10^{-3} M/sec

Determine: $\text{rate} = k[BrO_3^{-1}]^a[Br^{-1}]^b[H^{+1}]^c$

Find the numerical value of the specfic rate constant, k.

Solve for a using data from experiments #2 &#1:

$$\left(\frac{0.20M}{0.10M}\right)^a = \frac{1.6\times10^{-3}\,M/sec}{8.0\times10^{-4}\,M/sec} \qquad (2.0)^a = 2.0 \qquad a = 1$$

Solve for b using data from experiments #3 &#2:

$$\left(\frac{0.20M}{0.10M}\right)^b = \frac{3.2\times10^{-3}\,M/sec}{1.6\times10^{-3}\,M/sec} \qquad (2.0)^b = 2.0 \qquad b = 1$$

Solve for c using data from experiments #4 &#1:

$$\left(\frac{0.20M}{0.10M}\right)^c = \frac{3.2\times10^{-3}\,M/sec}{8.0\times10^{-4}\,M/sec} \qquad (2.0)^c = 4.0 \qquad c = 2$$

$$\text{rate} = k[BrO_3^{-1}]^1[Br^{-1}]^1[H^{+1}]^2$$

Rate Law Determination - Method of Initial Rates

Example #2

Overall equation: $1\,BrO_3^{-1}(aq) + 5\,Br^{-1}(aq) + 6\,H^{+1}(aq) \longrightarrow 3\,Br_2(liq) + 3\,H_2O(liq)$

Expt. #	$[BrO_3^{-1}]_o$	$[Br^{-1}]_o$	$[H^{+1}]_o$	Measured initial rate
1	0.10M	0.10M	0.10M	8.0×10^{-4} M/sec
2	0.20M	0.10M	0.10M	1.6×10^{-3} M/sec
3	0.20M	0.20M	0.10M	3.2×10^{-3} M/sec
4	0.10M	0.10M	0.20M	3.2×10^{-3} M/sec

$$\text{rate} = k[BrO_3^{-1}]^1 [Br^{-1}]^1 [H^{+1}]^2$$

To solve for the numerical value of k, use the data from any one of the experiments:

From Expt. #1: $8.0\times10^{-4}\,\text{M/sec} = k(0.10\text{M})^1(0.10\text{M})^1(0.10\text{M})^2$

$$k = \frac{8.0\times10^{-4}\,\text{M/sec}}{1.0\times10^{-4}\,\text{M}^4} = 8.0\ (\text{M}^3\cdot\text{sec})^{-1}$$

Rate Law Determination - Method of Initial Rates

Example #3

Overall equation: $2\,NO(g) + 1O_2(g) \longrightarrow 2NO_2(g)$

Expt. #	$[NO]_o$	$[O_2]_o$	Measured initial rate
1	0.0100M	0.0100M	2.00×10^{-3} M/sec
2	0.0300M	0.0100M	1.80×10^{-2} M/sec
3	0.0250M	0.0250M	3.13×10^{-2} M/sec

Determine: $\text{rate} = k[NO]^q[O_2]^r$

Find the numerical value of the specfic rate constant, k.

Rate Law Determination - Method of Initial Rates

Example #3

Overall equation: $2\,NO(g) + 1O_2(g) \longrightarrow 2NO_2(g)$

Expt. #	$[NO]_o$	$[O_2]_o$	Measured initial rate
1	0.0100M	0.0100M	$2.00\text{x}10^{-3}$ M/sec
2	0.0300M	0.0100M	$1.80\text{x}10^{-2}$ M/sec
3	0.0250M	0.0250M	$3.13\text{x}10^{-2}$ M/sec

Determine: $\text{rate} = k[NO]^q[O_2]^r$

Find the numerical value of the specfic rate constant, k.

Solve for q using data from experiments #2 &#1:

$$\left(\frac{0.0300M}{0.0100M}\right)^q = \frac{1.80\text{x}10^{-2}\ M/sec}{2.00\text{x}10^{-3}\ M/sec} \qquad (3.00)^q = 9.00 \qquad q = 2$$

Rate Law Determination - Method of Initial Rates

Example #3

Overall equation: $2\,NO(g) + 1O_2(g) \longrightarrow 2NO_2(g)$

Expt. #	$[NO]_o$	$[O_2]_o$	Measured initial rate
1	0.0100M	0.0100M	$2.00\text{x}10^{-3}$ M/sec
2	0.0300M	0.0100M	$1.80\text{x}10^{-2}$ M/sec
3	0.0250M	0.0250M	$3.13\text{x}10^{-2}$ M/sec

Determine: $\text{rate} = k[NO]^q[O_2]^r$

Find the numerical value of the specfic rate constant, k.

Solve for q using data from experiments #2 &#1:

$$\left(\frac{0.0300M}{0.0100M}\right)^q = \frac{1.80\text{x}10^{-2}\ M/sec}{2.00\text{x}10^{-3}\ M/sec} \qquad (3.00)^q = 9.00 \qquad q = 2$$

Whereas the concentration of NO(g) is not a fixed value in any pair of experiments, the above approach cannot be used. Instead, use the data from experiments #3 & #1 in the following manner:

$$\left(\frac{3.13\text{x}10^{-2}\ M/sec}{2.00\text{x}10^{-3}\ M/sec}\right) = \frac{k[0.0250M]^2[0.0250M]^r}{k[0.0100M]^2[0.0100M]^r} \qquad 15.65 = (6.25)(2.50)^r \quad 2.50 = (2.50)^r$$

$$r = 1$$

$$\text{rate} = k[NO]^2[O_2]^1$$

Rate Law Determination - Method of Initial Rates

Example #3

Overall equation: $2\,NO(g) + 1O_2(g) \longrightarrow 2NO_2(g)$

Expt. #	$[NO]_o$	$[O_2]_o$	Measured initial rate
1	0.0100M	0.0100M	2.00×10^{-3} M/sec
2	0.0300M	0.0100M	1.80×10^{-2} M/sec
3	0.0250M	0.0250M	3.13×10^{-2} M/sec

$$\text{rate} = k[NO]^2[O_2]^1$$

To solve for the numerical value of k, use the data from any one of the experiments:

From Expt. #1: $2.0 \times 10^{-3}\,\text{M/sec} = k(0.0100\text{M})^2(0.0100\text{M})^1$

$$k = \frac{2.00 \times 10^{-3}\ \text{M/sec}}{(0.0100\text{M})^2(0.0100\text{M})^1} = 2.00 \times 10^{3}\ (\text{M}^2 \cdot \text{sec})^{-1}$$

Rate Law Determination - Method of Initial Rates

Example #4

Consider the hypothetical rxn: $1A + 2B + 3C \longrightarrow 3D$

Expt. #	$[A]_o$	$[B]_o$	$[C]_o$	Measured initial rate
1	0.10M	0.01M	0.05M	1.0×10^{-4} M/sec
2	0.10M	0.02M	0.10M	2.0×10^{-4} M/sec
3	0.10M	0.02M	0.20M	2.0×10^{-4} M/sec
4	0.20M	0.02M	0.05M	8.0×10^{-4} M/sec

Determine: $\text{rate} = k[A]^f[B]^g[C]^h$

Find the numerical value of the specfic rate constant, k.

Rate Law Determination - Method of Initial Rates

Example #4

Consider the hypothetical rxn: $1A + 2B + 3C \longrightarrow 3D$

Expt. #	$[A]_o$	$[B]_o$	$[C]_o$	Measured initial rate
1	0.10M	0.01M	0.05M	1.0×10^{-4} M/sec
2	0.10M	0.02M	0.10M	2.0×10^{-4} M/sec
3	0.10M	0.02M	0.20M	2.0×10^{-4} M/sec
4	0.20M	0.02M	0.05M	8.0×10^{-4} M/sec

Determine: $\text{rate} = k[A]^f[B]^g[C]^h$

Find the numerical value of the specfic rate constant, k.

Approach to take

First, look for a pair of experiments in which two of the three reactant concentrations are fixed while the third one changes.
Answer: Experiments #2 & #3
With the concentations of A and B fixed, the concentration of C is doubled. No change in the measured initial rate is observed.
Conclusion: The order for reactant C must be zero (h=0).

Rate Law Determination - Method of Initial Rates

Example #4

Consider the hypothetical rxn: $1A + 2B + 3C \longrightarrow 3D$

Expt. #	$[A]_o$	$[B]_o$	$[C]_o$	Measured initial rate
1	0.10M	0.01M	0.05M	1.0×10^{-4} M/sec
2	0.10M	0.02M	0.10M	2.0×10^{-4} M/sec
3	0.10M	0.02M	0.20M	2.0×10^{-4} M/sec
4	0.20M	0.02M	0.05M	8.0×10^{-4} M/sec

Solve for f using data from experiments #2 & #4 or #3 & #4:

$$\left(\frac{0.20M}{0.10M}\right)^f = \frac{8.0 \times 10^{-4}\ M/sec}{2.0 \times 10^{-4}\ M/sec} \qquad (2.0)^f = 4.0 \qquad f = 2$$

Solve for g using data from experiments #1 & #2 or #1 & #3:

$$\left(\frac{0.02M}{0.01M}\right)^g = \frac{2.0 \times 10^{-4}\ M/sec}{1.0 \times 10^{-4}\ M/sec} \qquad (2.0)^g = 2.0 \qquad g = 1$$

$$\text{rate} = k[A]^2[B]^1[C]^0$$

To solve for the numerical value of k, use the data from any one of the experiments:

From Expt. #4: $8.0 \times 10^{-4} M/sec = k(0.20M)^2(0.02M)^1(0.05M)^0$

$$k = \frac{8.0 \times 10^{-4}\ M/sec}{8.0 \times 10^{-4}\ M^3} = 1.0\ (M^2 \cdot sec)^{-1}$$

Rate Law Determination - Method of Initial Rates

Example #5

Consider the hypothetical rxn: $1P + 3Q + 2R \longrightarrow 2S + 1T$

Expt. #	$[P]_o$	$[Q]_o$	$[R]_o$	Measured initial rate
1	0.25M	0.30M	0.10M	1.30 M/sec
2	0.40M	0.30M	0.25M	8.13 M/sec
3	0.40M	0.50M	0.10M	2.17 M/sec
4	0.25M	0.40M	0.10M	1.73 M/sec
5	0.15M	0.20M	0.20M	3.47 M/sec

Determine: $\text{rate} = k[P]^x[Q]^y[R]^z$

Find the numerical value of the specfic rate constant, k.

Rate Law Determination - Method of Initial Rates

Example #5

Consider the hypothetical rxn: $1P + 3Q + 2R \longrightarrow 2S + 1T$

Expt. #	$[P]_o$	$[Q]_o$	$[R]_o$	Measured initial rate
1	0.25M	0.30M	0.10M	1.30 M/sec
2	0.40M	0.30M	0.25M	8.13 M/sec
3	0.40M	0.50M	0.10M	2.17 M/sec
4	0.25M	0.40M	0.10M	1.73 M/sec
5	0.15M	0.20M	0.20M	3.47 M/sec

Determine: $\text{rate} = k[P]^x[Q]^y[R]^z$

Find the numerical value of the specfic rate constant, k.

Approach to take

First, look for a pair of experiments in which two of the three reactant concentrations are fixed while the third one changes.
Answer: In experiments #1 & #4, the initial concentrations of P and R are 0.25M and 0.10M, respectively, while the initial concentration of Q and the initial rate change by a factor of 1.33:

$$\left(\frac{0.40M}{0.30M}\right)^y = \frac{1.73\ M/sec}{1.30\ M/sec} \qquad (1.33)^y = 1.33 \qquad y = 1$$

$$\text{rate} = k[P]^x[Q]^1[R]^z$$

Rate Law Determination - Method of Initial Rates

Example #5

Consider the hypothetical rxn: $1P + 3Q + 2R \longrightarrow 2S + 1T$

Expt. #	$[P]_o$	$[Q]_o$	$[R]_o$	Measured initial rate
1	0.25M	0.30M	0.10M	1.30 M/sec
2	0.40M	0.30M	0.25M	8.13 M/sec
3	0.40M	0.50M	0.10M	2.17 M/sec
4	0.25M	0.40M	0.10M	1.73 M/sec
5	0.15M	0.20M	0.20M	3.47 M/sec

$$\text{rate} = k[P]^x[Q]^1[R]^z$$

Next, note that no pair of experiments exists in which the initial concentrations of Q & R or Q & P are fixed while that of the third is varied. Consequently, the following approach, in which data from experiments #3 & #1 are compared, needs to be used:

$$\left(\frac{2.17\ \text{M/sec}}{1.30\ \text{M/sec}}\right) = \frac{k[0.40\text{M}]^x[0.50\text{M}]^1[0.10\text{M}]^z}{k[0.25\text{M}]^x[0.30\text{M}]^1[0.10\text{M}]^z} \qquad 1.67 = (1.60)^x(1.67)^1(1)^z$$

$$1.00 = (1.60)^x \qquad x = 0$$

$$\text{rate} = k[P]^0[Q]^1[R]^z$$

Rate Law Determination - Method of Initial Rates

Example #5

Consider the hypothetical rxn: $1P + 3Q + 2R \longrightarrow 2S + 1T$

Expt. #	$[P]_o$	$[Q]_o$	$[R]_o$	Measured initial rate
1	0.25M	0.30M	0.10M	1.30 M/sec
2	0.40M	0.30M	0.25M	8.13 M/sec
3	0.40M	0.50M	0.10M	2.17 M/sec
4	0.25M	0.40M	0.10M	1.73 M/sec
5	0.15M	0.20M	0.20M	3.47 M/sec

$$\text{rate} = k[P]^0[Q]^1[R]^z$$

Finally, solve for z using data from experiments #2 & #1(in which only a change in the initial concentration of reactant R affects the initial rate - Why is this so?):

$$\left(\frac{0.25M}{0.10M}\right)^z = \frac{8.13\,M/sec}{1.30\,M/sec} \qquad (2.5)^z = 6.25 \qquad z = 2$$

$$\text{rate} = k[P]^0[Q]^1[R]^2$$

To solve for the numerical value of k, use the data from any one of the experiments:

From Expt. #3: $2.17\,M/sec = k(0.40M)^0(0.50M)^1(0.10M)^2$

$$k = \frac{2.17\,M/sec}{5.0\text{x}10^{-3}M^3} = 434\,(M^2\cdot sec)^{-1}$$