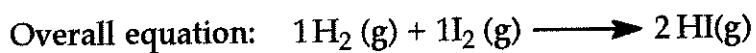


Rate Law Determination - Method of Initial Rates

Example #1



Expt. #	$[\text{H}_2]_0$	$[\text{I}_2]_0$	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: $\text{rate} = k[\text{H}_2]^x[\text{I}_2]^y$

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

Rate Law Determination - Method of Initial Rates

Example #1



Expt. #	$[\text{H}_2]_0$	$[\text{I}_2]_0$	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: $\text{rate} = k[\text{H}_2]^x[\text{I}_2]^y$

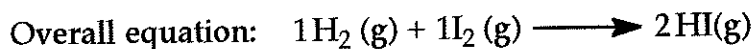
Find the numerical value of the specific rate constant, k.

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

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

Rate Law Determination - Method of Initial Rates

Example #1



Expt. #	$[\text{H}_2]_0$	$[\text{I}_2]_0$	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: $\text{rate} = k[\text{H}_2]^x[\text{I}_2]^y$

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

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

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

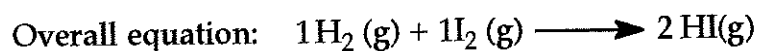
Solve for y using data from experiments #4 & #2:

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

$$\text{rate} = k[\text{H}_2]^1[\text{I}_2]^1$$

Rate Law Determination - Method of Initial Rates

Example #1



Expt. #	$[\text{H}_2]_0$	$[\text{I}_2]_0$	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

$$\text{rate} = k[\text{H}_2]^1 [\text{I}_2]^1$$

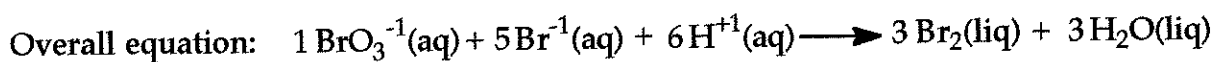
To solve for the numerical value of k , use the data from any one of the experiments:

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

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

Rate Law Determination - Method of Initial Rates

Example #2



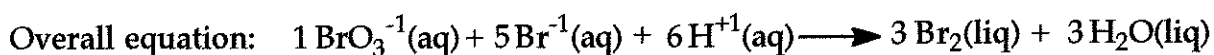
Expt. #	$[\text{BrO}_3^{-1}]_0$	$[\text{Br}^{-1}]_0$	$[\text{H}^{+1}]_0$	Measured initial rate
1	0.10M	0.10M	0.10M	$8.0 \times 10^{-4} \text{ M/sec}$
2	0.20M	0.10M	0.10M	$1.6 \times 10^{-3} \text{ M/sec}$
3	0.20M	0.20M	0.10M	$3.2 \times 10^{-3} \text{ M/sec}$
4	0.10M	0.10M	0.20M	$3.2 \times 10^{-3} \text{ M/sec}$

Determine: $\text{rate} = k[\text{BrO}_3^{-1}]^a [\text{Br}^{-1}]^b [\text{H}^{+1}]^c$

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

Rate Law Determination - Method of Initial Rates

Example #2



Expt. #	$[\text{BrO}_3^{-1}]_0$	$[\text{Br}^{-1}]_0$	$[\text{H}^{+1}]_0$	Measured initial rate
1	0.10M	0.10M	0.10M	$8.0 \times 10^{-4} \text{ M/sec}$
2	0.20M	0.10M	0.10M	$1.6 \times 10^{-3} \text{ M/sec}$
3	0.20M	0.20M	0.10M	$3.2 \times 10^{-3} \text{ M/sec}$
4	0.10M	0.10M	0.20M	$3.2 \times 10^{-3} \text{ M/sec}$

Determine: $\text{rate} = k[\text{BrO}_3^{-1}]^a [\text{Br}^{-1}]^b [\text{H}^{+1}]^c$

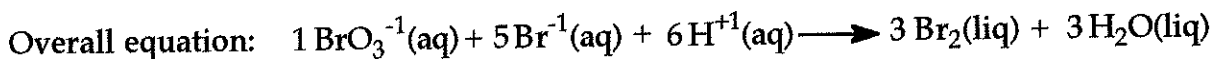
Find the numerical value of the specific rate constant, k.

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

$$\left(\frac{0.20\text{M}}{0.10\text{M}}\right)^a = \frac{1.6 \times 10^{-3} \text{ M/sec}}{8.0 \times 10^{-4} \text{ M/sec}} \quad (2.0)^a = 2.0 \quad a = 1$$

Rate Law Determination - Method of Initial Rates

Example #2



Expt. #	$[\text{BrO}_3^{-1}]_0$	$[\text{Br}^{-1}]_0$	$[\text{H}^{+1}]_0$	Measured initial rate
1	0.10M	0.10M	0.10M	$8.0 \times 10^{-4} \text{ M/sec}$
2	0.20M	0.10M	0.10M	$1.6 \times 10^{-3} \text{ M/sec}$
3	0.20M	0.20M	0.10M	$3.2 \times 10^{-3} \text{ M/sec}$
4	0.10M	0.10M	0.20M	$3.2 \times 10^{-3} \text{ M/sec}$

Determine: $\text{rate} = k[\text{BrO}_3^{-1}]^a [\text{Br}^{-1}]^b [\text{H}^{+1}]^c$

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

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

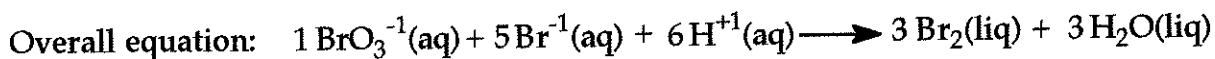
$$\left(\frac{0.20\text{M}}{0.10\text{M}}\right)^a = \frac{1.6 \times 10^{-3} \text{ M/sec}}{8.0 \times 10^{-4} \text{ M/sec}} \quad (2.0)^a = 2.0 \quad a = 1$$

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

$$\left(\frac{0.20\text{M}}{0.10\text{M}}\right)^b = \frac{3.2 \times 10^{-3} \text{ M/sec}}{1.6 \times 10^{-3} \text{ M/sec}} \quad (2.0)^b = 2.0 \quad b = 1$$

Rate Law Determination - Method of Initial Rates

Example #2



Expt. #	$[\text{BrO}_3^{-1}]_0$	$[\text{Br}^{-1}]_0$	$[\text{H}^{+1}]_0$	Measured initial rate
1	0.10M	0.10M	0.10M	$8.0 \times 10^{-4} \text{ M/sec}$
2	0.20M	0.10M	0.10M	$1.6 \times 10^{-3} \text{ M/sec}$
3	0.20M	0.20M	0.10M	$3.2 \times 10^{-3} \text{ M/sec}$
4	0.10M	0.10M	0.20M	$3.2 \times 10^{-3} \text{ M/sec}$

Determine: $\text{rate} = k[\text{BrO}_3^{-1}]^a [\text{Br}^{-1}]^b [\text{H}^{+1}]^c$

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

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

$$\left(\frac{0.20\text{M}}{0.10\text{M}}\right)^a = \frac{1.6 \times 10^{-3} \text{ M/sec}}{8.0 \times 10^{-4} \text{ M/sec}} \quad (2.0)^a = 2.0 \quad a = 1$$

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

$$\left(\frac{0.20\text{M}}{0.10\text{M}}\right)^b = \frac{3.2 \times 10^{-3} \text{ M/sec}}{1.6 \times 10^{-3} \text{ M/sec}} \quad (2.0)^b = 2.0 \quad b = 1$$

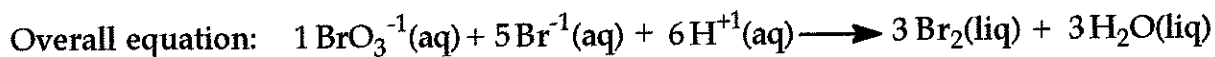
Solve for c using data from experiments #4 & #1:

$$\left(\frac{0.20\text{M}}{0.10\text{M}}\right)^c = \frac{3.2 \times 10^{-3} \text{ M/sec}}{8.0 \times 10^{-4} \text{ M/sec}} \quad (2.0)^c = 4.0 \quad c = 2$$

$$\text{rate} = k[\text{BrO}_3^{-1}]^1 [\text{Br}^{-1}]^1 [\text{H}^{+1}]^2$$

Rate Law Determination - Method of Initial Rates

Example #2



Expt. #	$[\text{BrO}_3^{-1}]_0$	$[\text{Br}^{-1}]_0$	$[\text{H}^{+1}]_0$	Measured initial rate
1	0.10M	0.10M	0.10M	$8.0 \times 10^{-4} \text{ M/sec}$
2	0.20M	0.10M	0.10M	$1.6 \times 10^{-3} \text{ M/sec}$
3	0.20M	0.20M	0.10M	$3.2 \times 10^{-3} \text{ M/sec}$
4	0.10M	0.10M	0.20M	$3.2 \times 10^{-3} \text{ M/sec}$

$$\text{rate} = k[\text{BrO}_3^{-1}]^1 [\text{Br}^{-1}]^1 [\text{H}^{+1}]^2$$

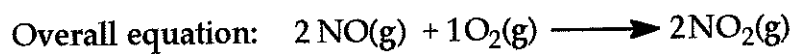
To solve for the numerical value of k , use the data from any one of the experiments:

From Expt. #1: $8.0 \times 10^{-4} \text{ M/sec} = k(0.10\text{M})^1 (0.10\text{M})^1 (0.10\text{M})^2$

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

Rate Law Determination - Method of Initial Rates

Example #3



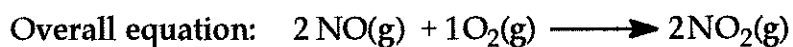
Expt. #	$[\text{NO}]_0$	$[\text{O}_2]_0$	Measured initial rate
1	0.0100M	0.0100M	2.00×10^{-3} M/sec
2	0.0300M	0.0100M	1.80×10^{-2} M/sec
3	0.0250M	0.0250M	3.13×10^{-2} M/sec

Determine: $\text{rate} = k[\text{NO}]^q [\text{O}_2]^r$

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

Rate Law Determination - Method of Initial Rates

Example #3



Expt. #	$[\text{NO}]_0$	$[\text{O}_2]_0$	Measured initial rate
1	0.0100M	0.0100M	$2.00 \times 10^{-3} \text{ M/sec}$
2	0.0300M	0.0100M	$1.80 \times 10^{-2} \text{ M/sec}$
3	0.0250M	0.0250M	$3.13 \times 10^{-2} \text{ M/sec}$

Determine: $\text{rate} = k[\text{NO}]^q [\text{O}_2]^r$

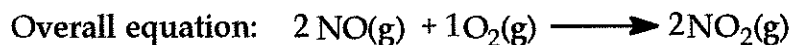
Find the numerical value of the specific rate constant, k.

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

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

Rate Law Determination - Method of Initial Rates

Example #3



Expt. #	$[\text{NO}]_0$	$[\text{O}_2]_0$	Measured initial rate
1	0.0100M	0.0100M	$2.00 \times 10^{-3} \text{ M/sec}$
2	0.0300M	0.0100M	$1.80 \times 10^{-2} \text{ M/sec}$
3	0.0250M	0.0250M	$3.13 \times 10^{-2} \text{ M/sec}$

Determine: $\text{rate} = k[\text{NO}]^q [\text{O}_2]^r$

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

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

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

Whereas the concentration of $\text{NO}(\text{g})$ 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:

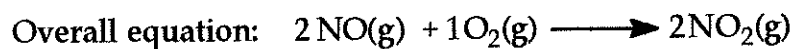
$$\left(\frac{3.13 \times 10^{-2} \text{ M/sec}}{2.00 \times 10^{-3} \text{ M/sec}} \right) = \frac{k[0.0250\text{M}]^2 [0.0250\text{M}]^r}{k[0.0100\text{M}]^2 [0.0100\text{M}]^r} \quad 15.65 = (6.25)(2.50)^r \quad 2.50 = (2.50)^r$$

$r = 1$

$$\text{rate} = k[\text{NO}]^2 [\text{O}_2]^1$$

Rate Law Determination - Method of Initial Rates

Example #3



Expt. #	$[\text{NO}]_0$	$[\text{O}_2]_0$	Measured initial rate
1	0.0100M	0.0100M	$2.00 \times 10^{-3} \text{ M/sec}$
2	0.0300M	0.0100M	$1.80 \times 10^{-2} \text{ M/sec}$
3	0.0250M	0.0250M	$3.13 \times 10^{-2} \text{ M/sec}$

$$\text{rate} = k[\text{NO}]^2 [\text{O}_2]^1$$

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 specific rate constant, k.

Rate Law Determination - Method of Initial Rates

Example #4

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

Expt. #	$[A]_0$	$[B]_0$	$[C]_0$	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 specific 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 concentrations 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. #	$[A]_0$	$[B]_0$	$[C]_0$	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:

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

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

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

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

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

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

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

Rate Law Determination - Method of Initial Rates

Example #5

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

Expt. #	$[P]_0$	$[Q]_0$	$[R]_0$	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 specific rate constant, k.

Rate Law Determination - Method of Initial Rates

Example #5

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

Expt. #	$[P]_0$	$[Q]_0$	$[R]_0$	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 specific 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:

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

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

Rate Law Determination - Method of Initial Rates

Example #5

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

Expt. #	$[P]_0$	$[Q]_0$	$[R]_0$	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:

$$\left(\frac{2.17 \text{ M/sec}}{1.30 \text{ M/sec}} \right) = \frac{k[0.40\text{M}]^x [0.50\text{M}]^1 [0.10\text{M}]^z}{k[0.25\text{M}]^x [0.30\text{M}]^1 [0.10\text{M}]^z} \quad \begin{aligned} 1.67 &= (1.60)^x (1.67)^1 (1)^z \\ 1.00 &= (1.60)^x \quad x = 0 \end{aligned}$$

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

Rate Law Determination - Method of Initial Rates

Example #5

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

Expt. #	$[P]_0$	$[Q]_0$	$[R]_0$	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?):

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

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

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

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

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