

Kinetics Problems

A reaction has a rate constant of $4.58 \times 10^3 \text{ s}^{-1}$.

- o Calculate the half-life (λ) of the reaction.
- o How many seconds are required for the concentration of the reactant to decrease by 15.4%.

$$\lambda = \frac{\ln 2}{k} = \frac{\ln 2}{4.58 \times 10^3 \text{ s}^{-1}} = 1.51 \times 10^{-4} \text{ s}$$

$$\ln[A]_t = -kt + \ln[A]_0$$

$$[A]_t = 0.846[A]_0$$

$$\ln(0.846[A]_0) = -kt + \ln[A]_0$$

$$\frac{\ln 0.846}{-k} = t = \frac{\ln 0.846}{-4.58 \times 10^3 \text{ s}^{-1}} = 3.65 \times 10^{-5} \text{ s}$$

A reaction ($A + 2B \rightarrow C$) has the following rate data:

$[A]_0/\text{M}$	$[B]_0/\text{M}$	Rate ₀ /M s ⁻¹
0.1523	0.0115	1.45
0.3051	0.0115	3.00
0.3051	0.0232	5.99

- Calculate the rate law for this reaction.
- Find the rate constant with the units.
- What is the rate of this reaction if $[A] = 0.1000 \text{ M}$ and $[B] = 0.0150 \text{ M}$?

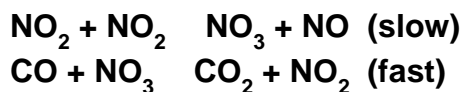
A doubles between 1 and 2 and so does the rate so the reaction is first order in A. B doubles between 2 and 3 and so does the rate so the reaction is first order in B. Rate law: rate = $k[A][B]$

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

$$k = \frac{\text{rate}}{[A][B]} = \frac{1.45 \text{ M s}^{-1}}{[0.1523 \text{ M}][0.0115 \text{ M}]} = 828 \text{ M}^{-1} \text{ s}^{-1}$$

$$\text{rate} = k[A][B] = (828 \text{ M}^{-1} \text{ s}^{-1})(0.1000 \text{ M})(0.0150 \text{ M}) = 1.24 \text{ M s}^{-1}$$

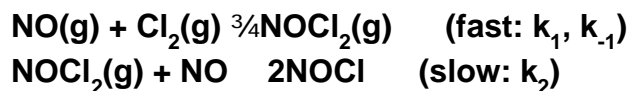
The reaction ($\text{CO} + \text{NO}_2 \rightarrow \text{CO}_2 + \text{NO}$) has the following proposed mechanism:



What is the predicted rate law for this reaction?

The first step is slow so the rate law is determined from this step.
 $\text{Rate} = k_1[\text{NO}_2]^2$.

The reaction ($2 \text{NO} + \text{Cl}_2 \rightarrow 2 \text{NOCl}_2$) has the following proposed mechanism:



Find the predicted mechanism for this reaction.

The second step is slow and gives a rate law of:

$$\text{rate} = k_2[\text{NOCl}_2][\text{NO}]$$

The intermediate must be eliminated from the rate law. This is done with the fast equilibrium in the first step.

$$k_1[\text{NO}][\text{Cl}_2] = k_{-1}[\text{NOCl}_2]$$

$$[\text{NOCl}_2] = \frac{k_1}{k_{-1}}[\text{NO}][\text{Cl}_2]$$

$$\text{rate} = k_2 \left(\frac{k_1}{k_{-1}}[\text{NO}][\text{Cl}_2] \right) [\text{NO}] = k[\text{NO}]^2[\text{Cl}_2]$$

A reaction has a rate constant of $4.53 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ at 22.5 C and $6.89 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ at 28.9 C. What is the rate constant at 25.0 C?

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$E_a = \frac{R \ln \frac{k_2}{k_1}}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} = \frac{(8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}) \ln \frac{6.89 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}}{4.53 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}}}{\left(\frac{1}{295.7 \text{ K}} - \frac{1}{302.1 \text{ K}} \right)} = 48.6 \text{ kJ mol}^{-1}$$

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln k_2 = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) + \ln k_1 = \frac{48.6 \text{ kJ mol}^{-1}}{(8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})} \left(\frac{1}{295.7 \text{ K}} - \frac{1}{298.2 \text{ K}} \right) + \ln 4.53 \times 10^{-2}$$

$$= -2.9287$$

$$k_2 = e^{-2.9287} = 5.35 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$$