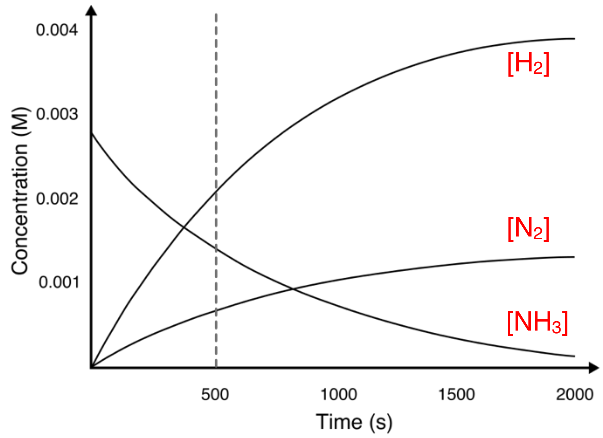
1. Consider the degradation of ammonia gas into nitrogen gas and hydrogen gas.

$$2\ NH_3\ (g) \rightarrow N_2\ (g) + 3\ H_2\ (g)$$

A) For the concentration vs. time plot to the right, label each curve with the appropriate chemical species.



Discuss how you chose each curve.

$[NH_3]$ decreases over time.
$[N_2]$ and $[H_2]$ increase over time.
$[H_2]$ increases more rapidly than $[N_2]$.

B) At t = 500 s, you determine the slope of a line tangent to the NH_3-curve to be -1.94×10^{-6} M/s. What is the rate of the reaction at this instant?

Recall that the instantaneous rate of the reaction can be expressed as

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[\mathrm{NH_3}]}{\Delta t} = \frac{\Delta[\mathrm{N_2}]}{\Delta t} = \frac{1}{3}\frac{\Delta[\mathrm{H_2}]}{\Delta t}$$

The slope of the tangent lines tells us how $[NH_3]$ changes with respect to time, so the rate is

$$\text{Rate} = -\frac{1}{2}\left(-1.94 \times 10^{-6}\,\frac{\mathrm{M}}{\mathrm{s}}\right) = 9.70 \times 10^{-7}\,\frac{\mathrm{M}}{\mathrm{s}} \quad \{3\text{ sig. figs.}\}$$

C) If you were to compare the slopes of the tangent lines for the N_2- and H_2-curves at t = 500 s, how do you think they compare quantitatively to the slope in part B for NH_3? Why?

From the answer to part B above, we can see that the slopes will be related by the stoichiometry of the balanced chemical equation. Therefore, the slopes of $[N_2]$ and $[H_2]$ can be related to $[NH_3]$ by

$$\frac{\Delta[\mathrm{N_2}]}{\Delta t} = -\frac{1}{2}\frac{\Delta[\mathrm{NH_3}]}{\Delta t} = 9.70 \times 10^{-7}\,\frac{\mathrm{M}}{\mathrm{s}} \qquad \frac{\Delta[\mathrm{H_2}]}{\Delta t} = -\frac{3}{2}\frac{\Delta[\mathrm{NH_3}]}{\Delta t} = 2.91 \times 10^{-6}\,\frac{\mathrm{M}}{\mathrm{s}}$$

2. The overall stoichiometry in parts A and B below are the same, but the rate laws differ.

A) Determine the rate law for the following reaction using the initial rates data.

$$2\ NO\ (g) + O_2\ (g) \rightarrow 2\ NO_2\ (g)$$

Experiment	$[NO]_o$ (M)	$[O_2]_o$ (M)	Initial Rate (M/s)
1	0.100	0.100	1.24
2	0.100	0.050	0.62
3	0.050	0.100	0.31

Our rate law will have the form: $\text{Rate} = k[\mathrm{NO}]^a[\mathrm{O_2}]^b$

Compare experiments 1 and 3 to find a, the order of the reaction with respect to [NO].
Compare experiments 1 and 2 to find b, the order of the reaction with respect to $[O_2]$.
Plug in the values from any one experiment (I choose #1) to solve for k.

$$\frac{\text{Rate}_1}{\text{Rate}_3} = \frac{k[\mathrm{NO}]_1^a[\mathrm{O_2}]_1^b}{k[\mathrm{NO}]_3^a[\mathrm{O_2}]_3^b} \qquad \frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k[\mathrm{NO}]_1^a[\mathrm{O_2}]_1^b}{k[\mathrm{NO}]_2^a[\mathrm{O_2}]_2^b}$$

$$\frac{\text{Rate}_1}{\text{Rate}_3} = \frac{[\mathrm{NO}]_1^a}{[\mathrm{NO}]_3^a} \qquad \frac{\text{Rate}_1}{\text{Rate}_2} = \frac{[\mathrm{O_2}]_1^b}{[\mathrm{O_2}]_2^b} \qquad \text{Rate}_1 = k[\mathrm{NO}]_1^2[\mathrm{O_2}]_1^1$$

$$\frac{1.24\,\frac{\mathrm{M}}{\mathrm{s}}}{0.31\,\frac{\mathrm{M}}{\mathrm{s}}} = \left(\frac{0.100\ \mathrm{M}}{0.050\ \mathrm{M}}\right)^a \qquad \frac{1.24\,\frac{\mathrm{M}}{\mathrm{s}}}{0.62\,\frac{\mathrm{M}}{\mathrm{s}}} = \left(\frac{0.100\ \mathrm{M}}{0.050\ \mathrm{M}}\right)^b \qquad 1.24\,\frac{\mathrm{M}}{\mathrm{s}} = k(0.100\ \mathrm{M})^2(0.100\ \mathrm{M})^1$$

$$4 = 2^a \qquad 2 = 2^b \qquad k = 1240\ \mathrm{M^{-2}s^{-1}}$$

$$a = 2 \qquad b = 1$$

Therefore, $\text{Rate} = k[\mathrm{NO}]^2[\mathrm{O_2}]^1;\ k = 1240\ \mathrm{M^{-3}s^{-1}}$

B) Determine the rate law for the following reaction using the initial rates data.

$$2\ NO\ (g) + Cl_2\ (g) \rightarrow 2\ NOCl\ (g)$$

Experiment	$[NO]_o$ (M)	$[Cl_2]_o$ (M)	Initial Rate (M/s)
1	0.200	0.100	0.63
2	0.200	0.300	5.70
3	0.800	0.100	2.58

Our rate law will have the form: $\text{Rate} = k[\text{NO}]^a[\text{Cl}_2]^b$

Compare experiments 3 and 1 to find a, the order of the reaction with respect to [NO].
Compare experiments 2 and 1 to find b, the order of the reaction with respect to [Cl_2].
Plug in the values from any one experiment (I choose #1) to solve for *k*.

$$\frac{\text{Rate}_3}{\text{Rate}_1} = \frac{k[\text{NO}]_3^a[\text{Cl}_2]_3^b}{k[\text{NO}]_1^a[\text{Cl}_2]_1^b} \qquad \frac{\text{Rate}_3}{\text{Rate}_1} = \frac{[\text{NO}]_3^a}{[\text{NO}]_1^a} \qquad \frac{2.58\,\frac{\text{M}}{\text{s}}}{0.63\,\frac{\text{M}}{\text{s}}} = \left(\frac{0.800\text{ M}}{0.200\text{ M}}\right)^a \qquad 4 = 4^a \qquad a = 1$$

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[\text{NO}]_2^a[\text{Cl}_2]_2^b}{k[\text{NO}]_1^a[\text{Cl}_2]_1^b} \qquad \frac{\text{Rate}_2}{\text{Rate}_1} = \frac{[\text{Cl}_2]_2^b}{[\text{Cl}_2]_1^b} \qquad \frac{5.70\,\frac{\text{M}}{\text{s}}}{0.63\,\frac{\text{M}}{\text{s}}} = \left(\frac{0.300\text{ M}}{0.100\text{ M}}\right)^b \qquad 9 = 3^b \qquad b = 2$$

$$\text{Rate}_1 = k[\text{NO}]_1^1[\text{Cl}_2]_1^2 \qquad 0.63\,\frac{\text{M}}{\text{s}} = k(0.200\text{ M})^1(0.100\text{ M})^2 \qquad k = 320\text{ M}^{-2}\text{s}^{-1}$$

If expt. 2 or 3: $k = 315\text{ M}^{-2}\text{s}^{-1}$

Therefore, $\text{Rate} = k[\text{NO}]^1[\text{Cl}_2]^2; k = 320\text{ M}^{-3}\text{s}^{-1}$ or $315\text{ M}^{-3}\text{s}^{-1}$

3. The following initial rate data was collected for the following chemical reaction:

$$2\ MnO_4^-\ (aq) + 5\ H_2C_2O_4\ (aq) + 6\ H^+\ (aq) \rightarrow 2\ Mn^{2+}\ (aq) + 10\ CO_2\ (g) + 8\ H_2O\ (l)$$

Experiment	$[MnO_4^-]_o$ (M)	$[H_2C_2O_4]_o$ (M)	$[H^+]_o$ (M)	Initial Rate (M/s)
1	1.0×10^{-3}	1.0×10^{-3}	1.0	2.0×10^{-4}
2	2.0×10^{-3}	1.0×10^{-3}	1.0	8.0×10^{-4}
3	2.0×10^{-3}	2.0×10^{-3}	1.0	1.6×10^{-3}
4	2.0×10^{-3}	2.0×10^{-3}	2.0	3.2×10^{-3}

A) Determine the rate law for this reaction.

Our rate law will have the form: $\text{Rate} = k[\text{MnO}_4^-]^2[\text{H}_2\text{C}_2\text{O}_4]^1[\text{H}^+]^1$

Compare experiments 2 and 1 to find a, the order of the reaction with respect to [MnO_4^-].
Compare experiments 3 and 2 to find b, the order of the reaction with respect to [$H_2C_2O_4$].
Compare experiments 4 and 3 to find c, the order of the reaction with respect to [H^+].

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[\text{MnO}_4^-]_2^a[\text{C}_2\text{O}_2\text{H}_4]_2^b[\text{H}^+]_2^c}{k[\text{MnO}_4^-]_1^a[\text{C}_2\text{O}_2\text{H}_4]_1^b[\text{H}^+]_1^c} \qquad \frac{\text{Rate}_2}{\text{Rate}_1} = \frac{[\text{MnO}_4^-]_2^a}{[\text{MnO}_4^-]_1^a} \qquad \frac{8.0\times10^{-4}\,\frac{\text{M}}{\text{s}}}{2.0\times10^{-4}\,\frac{\text{M}}{\text{s}}} = \left(\frac{2.0\times10^{-3}\text{ M}}{1.0\times10^{-3}\text{ M}}\right)^a \qquad 4 = 2^a \qquad a = 2$$

$$\frac{\text{Rate}_3}{\text{Rate}_2} = \frac{k[\text{MnO}_4^-]_3^a[\text{C}_2\text{O}_2\text{H}_4]_3^b[\text{H}^+]_3^c}{k[\text{MnO}_4^-]_2^a[\text{C}_2\text{O}_2\text{H}_4]_2^b[\text{H}^+]_2^c} \qquad \frac{\text{Rate}_3}{\text{Rate}_2} = \frac{[\text{C}_2\text{O}_2\text{H}_4]_3^b}{[\text{C}_2\text{O}_2\text{H}_4]_2^b} \qquad \frac{1.6\times10^{-3}\,\frac{\text{M}}{\text{s}}}{8.0\times10^{-4}\,\frac{\text{M}}{\text{s}}} = \left(\frac{2.0\times10^{-3}\text{ M}}{1.0\times10^{-3}\text{ M}}\right)^b \qquad 2 = 2^b \qquad b = 1$$

$$\frac{\text{Rate}_4}{\text{Rate}_3} = \frac{k[\text{MnO}_4^-]_4^a[\text{C}_2\text{O}_2\text{H}_4]_4^b[\text{H}^+]_4^c}{k[\text{MnO}_4^-]_3^a[\text{C}_2\text{O}_2\text{H}_4]_3^b[\text{H}^+]_3^c} \qquad \frac{\text{Rate}_4}{\text{Rate}_3} = \frac{[\text{H}^+]_4^c}{[\text{H}^+]_3^c} \qquad \frac{3.2\times10^{-3}\,\frac{\text{M}}{\text{s}}}{1.6\times10^{-3}\,\frac{\text{M}}{\text{s}}} = \left(\frac{2.0\text{ M}}{1.0\text{ M}}\right)^c \qquad 2 = 2^c \qquad c = 1$$

B) Determine the rate constant, including its units.

$$\text{Rate}_1 = k[\text{MnO}_4^-]_1^2[\text{C}_2\text{O}_2\text{H}_4]_1^b[\text{H}^+]_1^c$$

$$2.0\times10^{-4}\,\frac{\text{M}}{\text{s}} = k(1.0\times10^{-3}\text{ M})^2(1.0\times10^{-3}\text{ M})^1(1.0\text{ M})^1$$

$$k = 2.0\times10^5\text{ M}^{-3}\text{s}^{-1}\ \{2\text{ sig. figs}\}$$

C) Predict the initial reaction rate if $[MnO_4^-]_o = [H_2C_2O_4]_o = [H^+]_o = 1.5 \times 10^{-3}$ M?

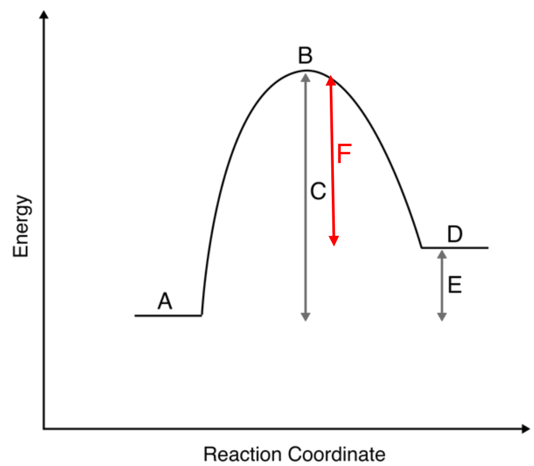
Because we know the rate law, including the value and units of the rate constant (k), we can evaluate the rate given any initial concentrations of our reactants.

$$\text{Rate} = k[\text{MnO}_4^-]^2[\text{H}_2\text{C}_2\text{O}_4]^1[\text{H}^+]^1$$

$$= \left(2.0 \times 10^5 \frac{1}{\text{M}^3\text{s}}\right)(1.5 \times 10^{-3}\text{ M})^2(1.5 \times 10^{-3}\text{ M})^1(1.5 \times 10^{-3}\text{ M})^1$$

$$\text{Rate} = 1.0 \times 10^{-6}\frac{\text{M}}{\text{s}}\ \{2\text{ sig. figs.}\}$$

4. Consider the following energy diagram.



A) Which letter corresponds to the activation energy for the reaction?

C: this is the minimum amount of energy needed for the reaction (A → D) to take place.

B) Which letter corresponds to the position of an "activated complex" or "transition state?"

B: this is the point at which our reaction reaches a critical geometry or orientation.

C) Is this reaction exothermic or endothermic? Which letter helps you decide this?

Endothermic; E: the product state is higher in energy than the reactant state.

D) In the energy diagram above, draw a new label (letter F) which corresponds to the activation energy for the reverse reaction.

See diagram.

E) Is the activation energy in the reverse direction greater than or less than the activation energy for the forward reaction?

Activation energy in the reverse direction is less than the activation energy in the forward direction.