1. Bromine can be produced by reacting bromate ions and bromide ions under acidic conditions:

$$BrO_3^-(aq) + 5\ Br^-(aq) + 6\ H^+(aq) \rightarrow 3\ Br_2(l) + 3\ H_2O(l)$$

A CHEM 154 student measured the initial reaction rates while changing the initial concentrations of the reactants (data shown at right). Determine the order of each of the reactants and the rate constant.

$$rate = k[BrO_3^-]^n[Br^-]^m[H^+]^p$$

Expt	Initial concentration (M)			Initial rate
	$[BrO_3^-]_0$	$[Br^-]_0$	$[H^+]_0$	(M/s)
1	0.25	0.25	0.25	4.6875×10^{-2}
2	0.50	0.25	0.25	9.375×10^{-2}
3	0.50	0.50	0.25	1.875×10^{-1}
4	0.25	0.25	0.5	1.875×10^{-1}

Taking the ratio of the rate law for experiment 1 divided by the rate law for experiment 2:

$$\frac{4.6875 \times 10^{-2}}{9.375 \times 10^{-2}} = \left(\frac{0.25\ M}{0.50\ M}\right)^n \rightarrow \frac{1}{2} = \left(\frac{1}{2}\right)^n \rightarrow n = 1$$

Taking the ratio of the rate law for experiment 2 divided by the rate law for experiment 3:

$$\frac{9.375 \times 10^{-2}}{1.875 \times 10^{-1}} = \left(\frac{0.25\ M}{0.50\ M}\right)^m \rightarrow \frac{1}{2} = \left(\frac{1}{2}\right)^m \rightarrow m = 1$$

Taking the ratio of the rate law for experiment 1 divided by the rate law for experiment 4:

$$\frac{4.6875 \times 10^{-2}}{1.875 \times 10^{-1}} = \left(\frac{0.25\ M}{0.50\ M}\right)^p \rightarrow \frac{1}{4} = \left(\frac{1}{2}\right)^p \rightarrow p = 2$$

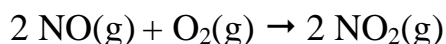**Use any experiment to determine the rate constant k. Using experiment 1:**

$$4.6875 \times 10^{-2}M\ s^{-1} = k[0.25\ M]^1[0.25\ M]^1[0.25\ M]^2 \rightarrow k = 12.0\ M^{-3}s^{-1}$$

Thus, the experimental rate law is

$$rate = k[BrO_3^-][Br^-][H^+]^2$$

with the value of the rate constant k given above.

2. **Good question.** A CHEM 154 student measured the initial rates of consumption of oxygen for the reaction

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

Expt.	$[NO]_0$ (M)	$[O_2]_0$ (M)	Initial rate (M/s)
1	1.66 x 10⁻³	1.66 x 10⁻³	3.32 x 10⁻⁵
2	4.98 x 10⁻³	1.66 x 10⁻³	2.99 x 10⁻⁴
3	4.15 x 10⁻³	4.15 x 10⁻³	5.20 x 10⁻⁴

a) Determine the rate law for this reaction.

$$Rate = k[NO]^n[O_2]^m$$

To determine the powers n and m, we take ratios of initial rates from different experiments in such a way as to isolate one power at a time.

Take the ratio of the data from experiment 2 to experiment 1:

$$\frac{2.99 \times 10^{-4} M/s}{3.32 \times 10^{-5} M/s} = \frac{k(4.98 \times 10^{-3} M)^n (1.66 \times 10^{-3} M)^m}{k(1.66 \times 10^{-3} M)^n (1.66 \times 10^{-3} M)^m}$$

$$9.006 = (3)^n \ \rightarrow \ \ln(9.006) = n \cdot \ln(3) \ \rightarrow \ n = 2$$

This can also be solved by inspection.

Take the ratio of the data from experiment 3 to experiment 2:

$$\frac{5.20 \times 10^{-4} M/s}{2.99 \times 10^{-4} M/s} = \frac{k(4.15 \times 10^{-3} M)^2 (4.15 \times 10^{-3} M)^m}{k(4.98 \times 10^{-3} M)^2 (1.66 \times 10^{-3} M)^m}$$

$$2.504 = (2.5)^m \ \rightarrow \ m = 1$$

Now take one of the experimental data points to calculate k, now that the powers in the rate law have been determined. Experiment 2 gives

$$2.99 \times 10^{-4} \frac{M}{s} = k(4.98 \times 10^{-3}\ M)^2 (1.66 \times 10^{-3}\ M)^1$$

$$k = 7.26 \times 10^3\ M^{-2}s^{-1}$$

b) What would be the initial rate for an experiment where $[NO]_0 = 1.03$ x 10^{-2} M and $[O_2]_0 = 1.22$ x 10^{-2} M?

$$Rate = 7.26 \times 10^3 M^{-2}s^{-1}(1.03 \times 10^{-2}M)^2(1.22 \times 10^{-2}M)^1 = 9.40 \times 10^{-3} Ms^{-1}$$

3. An environmental engineer recorded the following data for changes in concentration of NO_2 as a function of time.

   a) Complete the table to the right and plot each of the results as a function of time below.

Time (s)	$[NO_2]$ (M)	$\ln[NO_2]$	$1/[NO_2]$
0.0	2.5×10^{-1}	**-1.39**	**4**
15.0	7.0×10^{-3}	**-4.96**	**143**
30.0	3.5×10^{-3}	**-5.65**	**286**
45.0	2.5×10^{-3}	**-5.99**	**400**
60.0	2.0×10^{-3}	**-6.21**	**500**

Plot $[NO_2]$ vs. time. If plot is linear then the reaction is zeroth order.
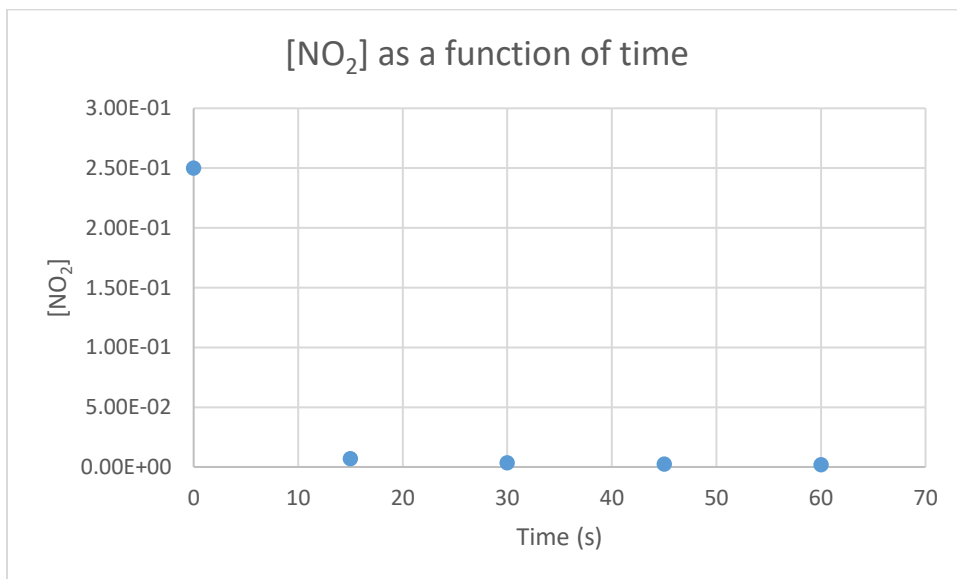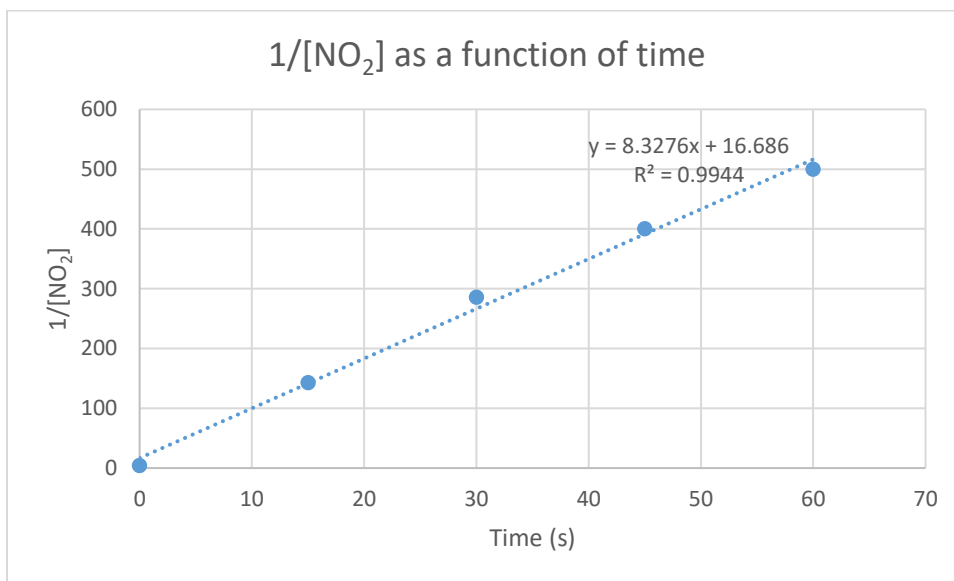

The plot is not linear, therefore the reaction is not zeroth order in NO_2

Plot $\ln [NO_2]$ vs. time. If plot is linear then the reaction is first order.
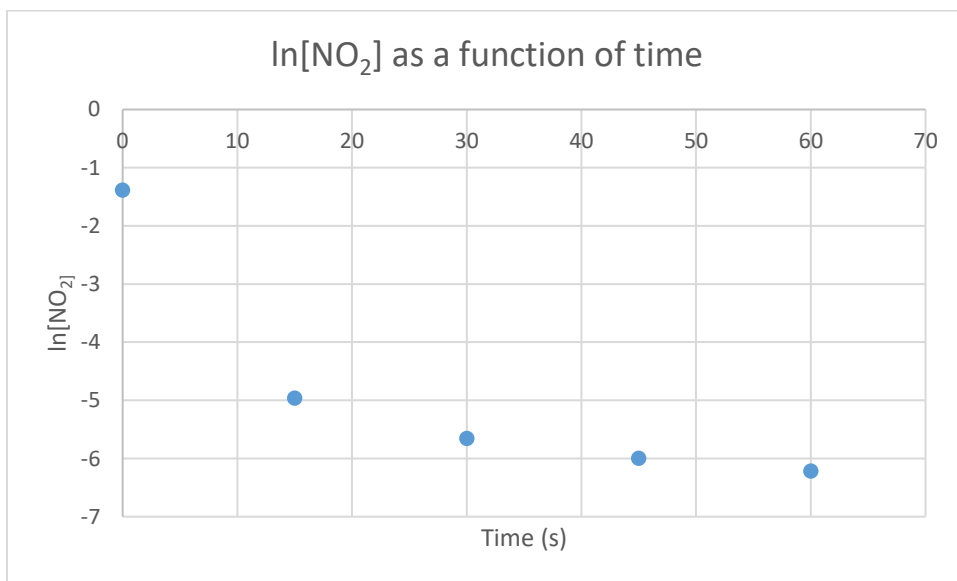
The plot is not linear, therefore the reaction is not first order in NO_2

Plot $1/[NO_2]$ vs. time. If plot is linear then the reaction is 2nd order.

$1/[NO_2]$ as a function of time

$y = 8.3276x + 16.686$
$R^2 = 0.9944$

The plot is linear, therefore the reaction is second order in NO_2

    b) Based on your results, what is the order of the reaction with respect to NO_2?

2nd order

    c) Calculate the rate constant, k, and write the rate law for NO_2.

k = slope = 8.33 M^{-1} s^{-1}

rate = $8.33 \text{ M}^{-1}\text{s}^{-1}[NO_2]^2$

4. Technetium-99m (^{99m}Tc) is a radioactive isotope commonly used for medical imaging. ^{99m}Tc undergoes first-order decomposition so that, 24 h after administration, only 6.25% of the original dose remains.

    a) What is the half-life (in hours) of the decomposition of ^{99m}Tc?

Starting with 100% of ^{99m}Tc (= 1 in the first order rate law equation below)

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

$$\ln[0.0625] = -k(24\text{h}) + \ln(1) \quad \rightarrow \quad k = 0.116 \text{ h}^{-1}$$

$$t_{\frac{1}{2}} = \frac{\ln(2)}{k} = \frac{\ln(2)}{0.116 \text{ h}^{-1}} = 6 \text{ h}$$

b) If a patient takes a 0.010 g dose of ^{99m}Tc for a functional brain imaging scan, how much (in grams) will remain in the radioactive form after one week?

$$\ln A = -0.116 \text{ h}^{-1}\left(7 \text{ days } \times \frac{24 \text{ hours}}{1 \text{ day}}\right) + \ln(0.010) = -24.013$$

$$A = 3.725 \times 10^{-11}\text{g}$$

Alternatively one could say 1 week = 7x(4 half lives) = 28 half lives so

$$\text{Mass,}_{Tc} = (0.010 \text{ g})\left(\frac{1}{2}\right)^{28} = 3.7 \text{ x } 10^{-11} \text{ g}$$

5. The following rate constants were obtained in an experiment in which the decomposition of gaseous N_2O_5 to form NO_2 and NO_3 was studied as a function of temperature. Determine E_a for this reaction in kJ/mol.

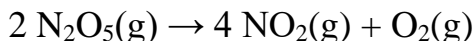| k (s^{-1})	T (K)	ln k	1/T (K^{-1})
7.0 x 10^{-7}	275	-14.172	0.003636
2.5 x 10^{-5}	295	-10.597	0.003390
5.0 x 10^{-4}	315	-7.601	0.003175
7.5 x 10^{-3}	335	-4.893	0.002985

Determine the slope between two points in the data set. In this solution, we will take the slope between the first and last data points:

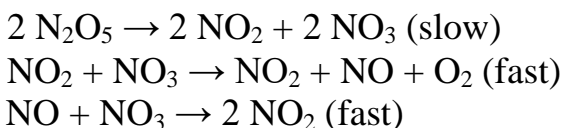$$-\frac{E_a}{R} = \frac{-4.89 + 14.17}{(0.002985 - 0.003636)\text{K}^{-1}} = -14255.9 \text{ K}$$

$$E_a = -14255.9 \text{ K} \times \left(-8.314 \frac{\text{J}}{\text{K mol}}\right) \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 118.52 \text{ kJ/mol}$$

Using a line of best-fit with ALL of the data provided, the activation energy is 118.28 kJ/mol. Either answer/method would be acceptable.

6. Dinitrogen pentoxide (N_2O_5) is one of the molecules responsible for ozone depletion in our atmosphere. As an environmental engineer you're interested in studying the mechanism of decomposition of N_2O_5 into NO_2 and O_2. The overall reaction is:

$$2 \text{ N}_2\text{O}_5(g) \rightarrow 4 \text{ NO}_2(g) + \text{O}_2(g)$$

You propose the following mechanism: $2 \text{ N}_2\text{O}_5 \rightarrow 2 \text{ NO}_2 + 2 \text{ NO}_3$ (slow)
$\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO}_2 + \text{NO} + \text{O}_2$ (fast)
$\text{NO} + \text{NO}_3 \rightarrow 2 \text{ NO}_2$ (fast)

a) Is this a reasonable mechanism to explain the decomposition of N_2O_5? Briefly explain your answer.

Yes, this a reasonable mechanism; steps add-up to give the overall reaction.

b) Identify all intermediates in your proposed mechanism.

NO_3 and NO

c) Identify the molecularity in each of the steps of the proposed mechanism.

All steps are bimolecular.

7. Given the information at right (measured at 298 K), sketch a G° vs. reaction progress diagram for the decomposition of N_2O_5 at 298 K. Assume the proposed mechanism is correct.

	$N_2O_5(g)$	$NO_2(g)$	$O_2(g)$
$\Delta H_f°$ (kJ / mol)	11	34	
$S_m°$ (J /mol K)	356	240	205

$$\Delta G° = \Delta H° - T\Delta S°$$

$$= 114\ \text{kJ} - 298\ \text{K} \times 0.453\ \frac{\text{kJ}}{\text{K}}$$

$$= -21\ \text{kJ}$$

The key to this plot is that the free energy of the products must be less than the reactants (reaction is exergonic). Also, the activation energy for the first step must be the highest of all three activation energies since this reaction is the slowest. Relative energies of intermediates are arbitrary.
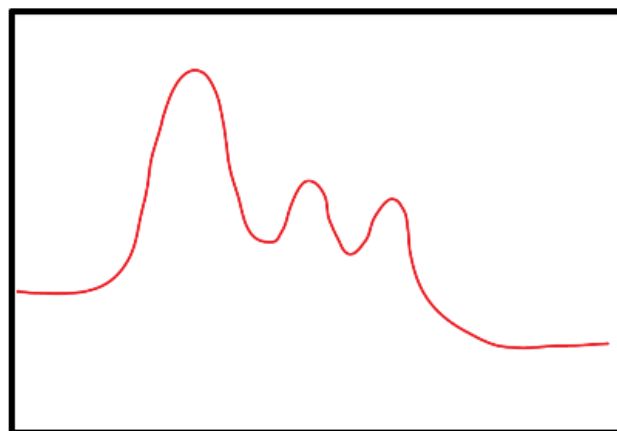
Reaction progress

8. **Good Question.** Will the sketch of enthalpy vs. reaction progress look the same as that of Q7? Briefly explain why or why not.

No, the plot of enthalpy vs. reaction progress will look different. This is because the reaction is endothermic. Therefore, the enthalpy of the products must be higher than that of the reactants.

For a challenge, try making your answers to Q7 and Q8 quantitative.