



Kinetics Practice – Supplemental Worksheet **KEY**

Determining reaction mechanism based on initial rate data

1. A reaction has the experimental rate law, $\text{rate} = k[A]^2$.
- a. How will the rate change if the concentration of a is tripled?

If $\text{rate}_1 = k[A]^2$, then $\text{rate}_2 = k[3A]^2 = 3^2 * k[A]^2 = 9 * k[A]^2 = 9 * \text{rate}_1$.
So the rate would be 9 times faster.

- b. How will the rate change if the concentration of A is halved?

If $\text{rate}_1 = k[A]^2$, then $\text{rate}_2 = k[\frac{1}{2}A]^2 = (\frac{1}{2})^2 * k[A]^2 = \frac{1}{4} * k[A]^2 = \frac{1}{4} * \text{rate}_1$.
So the rate would decrease. It would be a fourth of the original rate.

2. A reaction has the experimental rate law, $\text{rate} = k[A]$.
- a. How will the rate change if the concentration of a is tripled?

If $\text{rate}_1 = k[A]$, then $\text{rate}_2 = k[3A] = 3 * k[A] = 3 * \text{rate}_1$.
So the rate would be 3 times faster.

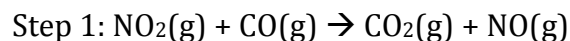
- b. How will the rate change if the concentration of A is halved?

If $\text{rate}_1 = k[A]$, then $\text{rate}_2 = k[\frac{1}{2}A] = (\frac{1}{2}) * k[A] = \frac{1}{2} * \text{rate}_1$.
So the rate would decrease. It would be one half of the original rate.

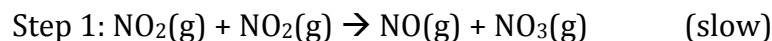


3. Three mechanisms for the reaction $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{NO}(\text{g})$ have been proposed:

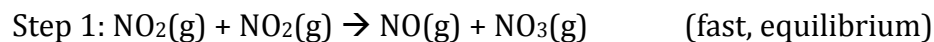
a. Mechanism A



b. Mechanism B



c. Mechanism C



Which mechanism agrees with the following initial rate data:

Experiment number	Initial $[\text{NO}_2]$ (mol/L)	Initial $[\text{CO}]$ (mol/L)	Initial Rate (M/s)
1	0.133	0.074	0.144
2	0.399	0.074	1.296
3	0.133	0.370	0.144

These types of problems can be tackled in a three steps

- Step 1: What is the rate law that matches up with the initial rate data given?

We see that when we triple the NO_2 concentration, the rate is 9 times greater. This means the reaction is second order with respect to NO_2 .

We see that when we increase the concentration of CO by 5 times, the rate does not change. This means the reaction is zero order with respect to CO . Thus, the experimental rate law is $\text{rate} = k[\text{NO}_2]^2$

- Step 2: What are the rate laws of the proposed mechanisms?

Mechanism A: $\text{rate} = k_a[\text{NO}_2][\text{CO}]$

Mechanism B: $\text{rate} = k_b[\text{NO}_2]^2$

Mechanism C: $\text{rate} = k_c[\text{NO}_3][\text{CO}]$ (We do not need to solve this further to eliminate the intermediates because we know that $[\text{CO}]$ is not in the experimental rate law. Thus, this mechanism does not agree with the experimental data.)

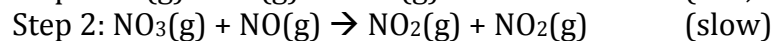
- Step 3: Which mechanism matches up with the experimental rate law?

The rate law for mechanism B and the experimental rate law match up. So, mechanism B agrees with the initial rate data.

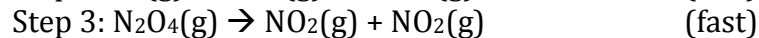
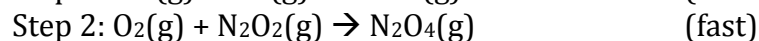
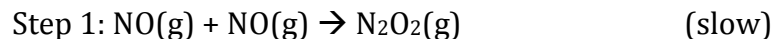


4. Three mechanisms for the reaction $O_2(g) + 2 NO(g) \rightarrow 2 NO_2(g)$ have been proposed:

a. Mechanism A



b. Mechanism B



Which mechanism agrees with the following initial rate data:

Experiment number	Initial $[O_2]$ (mol/L)	Initial $[NO]$ (mol/L)	Initial Rate (M/s)
1	0.210	0.122	0.136
2	0.420	0.122	0.272
3	0.210	0.244	0.544

- **Step 1:** What is the rate law that matches up with the initial rate data given?

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

- **Step 2:** What are the rate laws of the proposed mechanisms?

Mechanism A: $\text{rate}_a = k_a[O_2][NO_2]^2$ because

$$\text{rate}_{\text{slow}} = k_{\text{slow}}[NO][NO_3] \text{ and } K_{\text{step1}} = \frac{[NO_3]}{[O_2][NO]}$$

$$\text{so } [NO_3] = K_{\text{step1}}[O_2][NO]$$

$$\text{so } \text{rate}_a = k_a[O_2][NO]^2 \text{ where } k_a = k_{\text{slow}} * K_{\text{step1}}$$

Mechanism B: $\text{rate}_b = k_b[NO]^2$

- **Step 3:** Which mechanism matches up with the experimental rate law?

The rate law for mechanism A and the experimental rate law match up. So, mechanism A agrees with the initial rate data.

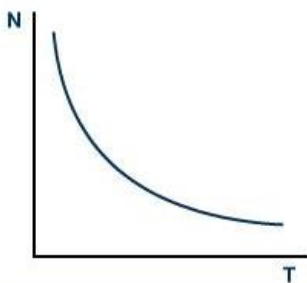
Going from rate laws to the integrated rate equations

5. The rate law for the reaction $\text{C}_4\text{H}_9\text{Cl} + \text{H}_2\text{O} \rightarrow \text{C}_4\text{H}_9\text{OH} + \text{HCl}$ is $\text{rate} = k[\text{C}_4\text{H}_9\text{Cl}]$.
- a. What would the integrated rate equation look like for this reaction?

$$[\text{C}_4\text{H}_9\text{Cl}](t) = [\text{C}_4\text{H}_9\text{Cl}]_0 e^{-kt}$$

- b. How would a plot of this equation look?

It would be an exponential decay graph similar to



- c. How could you find k from the plot?

To find k , you would need to plot $\ln([\text{C}_4\text{H}_9\text{Cl}](t))$ vs. t (time).
 This will be a straight line with the equation, $\ln([\text{C}_4\text{H}_9\text{Cl}](t)) = \ln[\text{C}_4\text{H}_9\text{Cl}]_0 - kt$.
 Thus, the slope = $-k$, so $k = -\text{slope}$.

6. The rate law for the reaction $2 \text{NO}_2 \rightarrow 2 \text{NO} + \text{O}_2$ is $\text{rate} = k[\text{NO}_2]^2$.

- a. What would the integrated rate equation look like for this reaction?

$$\frac{1}{[\text{NO}_2](t)} = \frac{1}{[\text{NO}_2]_0} + kt$$

- b. How would a plot of this equation look?

A plot of $\frac{1}{[\text{NO}_2](t)}$ vs. t (time), would be a straight line with the equation, $\frac{1}{[\text{NO}_2](t)} = \frac{1}{[\text{NO}_2]_0} + kt$

- c. How could you find k from the plot?

With the above plot, slope = k , so $k = \text{slope}$.



Activation Energy

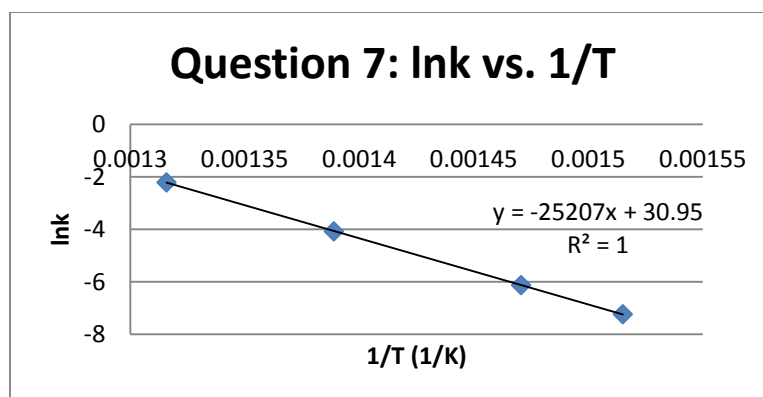
7. Given the data below for the reaction of the decomposition of iodoethane into ethane and hydrogen iodide,

T (K)	k (s ⁻¹)
660	7.2 * 10 ⁻⁴
680	2.2 * 10 ⁻³
720	1.7 * 10 ⁻²
760	0.11

- a. Calculate the activation energy for the reaction.

These types of problems can be tackled in a two steps

- Step 1:** Make an Arrhenius plot, lnk vs. 1/T
To make an Arrhenius plot, you need to enter this data into an excel spreadsheet, have excel calculate lnk and 1/T, make a scatterplot of lnk vs. 1/T and finally have excel display the trendline and its equation.



- Step 2:** Calculate E_a using the slope of the line
You need the Arrhenius plot because it gives you the line which has the generic equation $\ln k = \ln A - \left(\frac{E_a}{R}\right) \left(\frac{1}{T}\right)$.
So, the slope of the line in your plot is equal to $-\frac{E_a}{R}$. So, E_a = slope*(-R).
Thus, E_a = slope*(-R) = (-25207 K)(-8.314 J K⁻¹ mol⁻¹) = 2.1*10⁵ J/mol = 2.1*10² kJ/mol.

- b. What is the value of the rate constant at 400 °C?

$$400\text{ }^{\circ}\text{C} = 673\text{ K}$$

$$\text{So, } \ln k = \ln A - \left(\frac{E_a}{R}\right) \left(\frac{1}{T}\right) = 30.95 - 25207 \left(\frac{1}{673}\right) = -6.5047$$

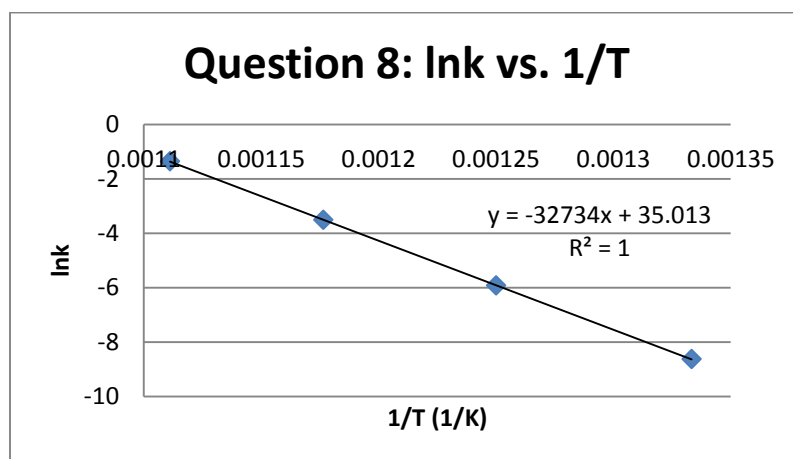
$$\text{So, } k = e^{-6.5047} = 0.0015 = 1.5 * 10^{-3} \text{ s}^{-1}$$

8. Given the data below for the reaction of the conversion of cyclopropane into propene,

T (K)	k (s ⁻¹)
750	1.8 * 10 ⁻⁴
800	2.7 * 10 ⁻³
850	3.0 * 10 ⁻²
900	0.26

- a. Calculate the activation energy for the reaction.

- **Step 1:** Make an Arrhenius plot, lnk vs. 1/T



- **Step 2:** Calculate E_a using the slope of the line

$$E_a = \text{slope} * (-R) = (-32734 \text{ K})(-8.314 \text{ J K}^{-1} \text{ mol}^{-1}) = 2.7 * 10^5 \text{ J/mol} = 2.7 * 10^2 \text{ kJ/mol.}$$

- b. What is the value of the rate constant at 600 °C?

$$600 \text{ °C} = 873 \text{ K}$$

$$\text{So, } \ln k = \ln A - \left(\frac{E_a}{R}\right) \left(\frac{1}{T}\right) = 35.01 - 32734 \left(\frac{1}{873}\right) = -2.4860$$

$$\text{So, } k = e^{-2.4860} = 0.083 = 8.3 * 10^{-2} \text{ s}^{-1}$$