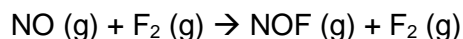


Problem Set 5**(Due: March 10th 5:00 PM)**

1. The gas phase decomposition of N_2O_4 to NO_2 is a first order reaction. Use the following data to answer each of the following questions:

Experiment	Temperature ($^{\circ}\text{C}$)	Initial $[\text{N}_2\text{O}_4]$ (M)	Initial Rate (M s^{-1})
1	25	0.1	5×10^3
2	40	0.15	2.3×10^4

- Determine the rate constant at 25°C .
 - Calculate the activation energy.
 - Calculate the pre-exponential factor.
 - What is the rate constant at 85°C ?
 - How much N_2O_4 will be left if 100 mM is allowed to decompose for 15 μs ? What concentration of NO_2 has been created?
 - How long will it take for 50% of the N_2O_4 in experiment 2 to decay? Report your answer in μs .
2. Sketch a reaction coordinate and clearly label the activation energy. On the same sketch, show a catalyzed reaction pathway. Why does a catalyst increase the rate of a reaction?
3. The following reaction has an activation energy of 6.3 kJ mol^{-1} and a pre-exponential factor of $6.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$.



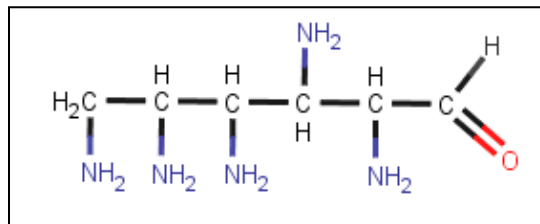
- What is the order of this reaction? Recall that A has the same units as the rate constant.
 - Calculate the rate constant at 25°C .
 - The product of this reaction is nitrosyl fluoride. This compound is typically written as NOF, but different arrangements of atoms are possible. Draw the correct Lewis structure for nitrosyl fluoride (make sure to consider atom arrangement and formal charge).
 - What is the molecular geometry of NOF?
4. Lactate dehydrogenase (LDH) is responsible for converting pyruvate to lactic acid. This is an important reaction during anaerobic respiration. The product is the reason why your muscles get sore after an intense workout.
- Look up the structures of lactic acid and pyruvate and sketch them.
 - LDH needs to be able to bind to pyruvate for a reaction to occur (i.e. to make an ES complex). Predict what the active site of the enzyme might look like so that it will recognize and bind to pyruvate.
 - Using the following experimental data for an **uncatalyzed first order reaction**, determine the rate law of this reaction (including the rate constant). You should be able to copy and paste this data directly into Excel.
 - How much lactic acid will be produced in 2 seconds if the starting concentration of pyruvate is 10 mM?

Time (min)	[Pyruvate] (M)
0	1.025
2	1.023
4	1.022
6	1.020
8	1.019
10	1.017
12	1.016
14	1.015

- An enzyme catalyze reaction ($[E]_{\text{total}} = 100 \text{ nM}$) has a K_M of $100 \text{ }\mu\text{M}$ and V_{max} of 15 nM min^{-1} . Determine the turnover number and catalytic efficiency.
- Using LeChatlier's principle to guide your answer, discuss why K_M changes when a competitive inhibitor is added to an enzyme reaction. Do the same for an uncompetitive inhibitor.
- Hexokinase is an enzyme that catalyzes the first step in glycolysis, the conversion of glucose to glucose-6-phosphate. However, this enzyme can also use a number of other sugars as substrates. These sugars only differ by the orientation of an alcohol group on the carbon backbone. The table below summarizes the structures and kinetic information about each sugar.

	Structure	k_{cat} (s^{-1})	K_M (mM)
Fructose		3.69	5.2
Glucose		5.01	0.023
Mannose		3.78	0.03

- Compare glucose to fructose. Are these structural or stereoisomers?
 - Which substrate will bind to hexokinase with the highest affinity?
 - How many molecules of glucose will be converted to product in two minutes? How about mannose?
 - Compare the structures of these three sugars. Why do you think that fructose has such a different K_M ?
 - Glucosamine is a suspected inhibitor of hexokinase. Below are plots of data collected with (orange line) and without (blue line) 20 mM glucosamine added.
 - Is glucosamine an inhibitor of hexokinase?
 - What type of inhibitor is this? How do you know?
 - Determine K_i
 - ADP is an uncompetitive inhibitor of hexokinase.
 - What does this mean?
 - Sketch a Lineweaver Burk that shows an experiment that is inhibited by ADP compared to an uninhibited reaction.
8. Explain why this molecule could be a good competitive inhibitor of hexokinase.



Graphs for Problem 7e:

