## Kinetics, Equilibrium & Catalysis

The rates of chemical reactions as a function of temperature will be discussed via the use of light sticks at 3 different temperatures and the  $H_2/O_2$  balloon explosion. The concept of activation barriers to chemical reactions will thus be introduced. The catalytic decomposition of  $H_2O_2$  and oscillating Iodine reaction will also be performed along with the chemical principles involved.

*Stuff:* \* thermos bottle (or insulated container) (you provide)

- \* boiling hot water to put in thermos (you provide)
- \* ice (you provide)
- \* water in container (you provide)
- \* large disposable plastic or aluminum tray (e.g., turkey pan) (you provide)
- \* roll of paper towels for cleaning up messes (you provide)
- \* small amount of dishwashing detergent liquid (you provide)

Propane torch (*we provide*, *please return*)

2 large plastic graduated cylinders (we provide, please clean & return)

 $3 \times 250$  mL beakers for the light sticks (*we provide, please return*)

3 light sticks (*we will provide*)

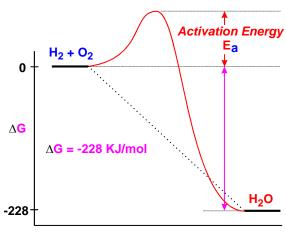
balloons – H<sub>2</sub>, O<sub>2</sub> and several H<sub>2</sub>/O<sub>2</sub> mixtures (*we provide*)

potassium iodide solution, dilute & concentrated (*we provide, return empty containers*) 15% and 30% H<sub>2</sub>O<sub>2</sub> (hydrogen peroxide) solution (*we provide, return empty containers*) oscillating iodine clock reaction kit (*we provide – return empty containers*) 600 mL beaker for oscillating clock rxn (*we provide - please clean & return*)

**General SAFETY notes:** You are representing LSU. Please be professional and safety conscious. 90% of safety is using good common sense and being cautious. Wear safety glasses when working with chemicals. Store the 15 and 30%  $H_2O_2$  and oscillating iodine clock Solution A (15%  $H_2O_2$ ) in a refrigerator if you pick up the chemicals the day before the demo. You need to practice the experiment before attempting it as a class demonstration. You will gain confidence and appear more professional to your audience.

**H**<sub>2</sub>/**O**<sub>2</sub> **balloon experiment:** You have three small balloons, one with pure oxygen, one with pure hydrogen, and one (several) with a 2:1 H<sub>2</sub>/O<sub>2</sub> mixture. Tie the balloon to the end of a yardstick and use a propane torch (or extra-long butane stick lighter) to ignite the O<sub>2</sub> balloon, the H<sub>2</sub> balloon, and finally the H<sub>2</sub>/O<sub>2</sub> balloon. Make sure that the balloons and torch are at arms length when you ignite them. The H<sub>2</sub>/O<sub>2</sub> balloon with detonate <u>extremely loudly</u>. *PLEASE WARN THE TEACHER AND SCHOOL ABOUT THIS BEFORE HAND – you may want to do this outside*. If you do it inside, don't let the balloon get too close to the ceiling. That is why the balloons are not very large.

Discuss how the reaction of  $H_2$  and  $O_2$  is spontaneous, that is, thermodynamically very downhill. Even though this reaction wants **-228** to take place it doesn't until you add some energy (the flame). Sketch out the energy diagram and discuss the activation barrier and how it stops reactants from reacting immediately.



**Reaction Coordinate** 

**Light sticks & Temperature experiment:** put ice water in one beaker, room temperature water in the second, and hot (not boiling) water from the thermos in the third. Put one light stick in each beaker and let sit for 5 mins (do this before you start the  $H_2/O_2$  balloon experiment). Now you can bend and snap them to activate them. The light sticks will glow at very different intensities corresponding to the temperature of the water that it they are sitting in (the hotter the temperature the faster the chemical reaction that makes the light). Discuss the effect that temperature has on the rate of chemical reactions and how it ties into the activation barrier (previous demo). Ask them which light stick will

use up the chemicals reacting to make the light first. Discuss the concept that the faster the reaction the sooner you use up all the reactants and the reaction will stop.

Bring up the old wives tale "*feed a fever, starve a cold*" or is it "*starve a fever, feed a cold*." Ask the students about which one they think is more correct with respect to the fever (ignore the cold part of the saying). Discuss the effect that a fever has on the body and how the higher temperature is the body's way of speeding up your metabolism to get your immune system working at a higher rate. The faster your metabolism, the more food you need to support it. Unfortunately, you tend to lose your appetite when you have a fever. So a fever is your body's way of speeding up your immune system to fight off infections and disease. Naturally, if the fever goes too high for too long you will die. Similarly, if your body temperature drops more than about 6° F all the chemical reactions slow down enough that you can die (hypothermia).

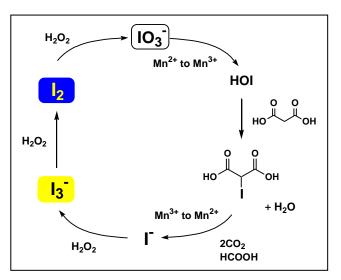
**Catalytic decomposition of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>):** Pour the 30% H<sub>2</sub>O<sub>2</sub> (careful: this is relatively concentrated hydrogen peroxide and is potentially dangerous – wear safety glasses) into the one graduated cylinder, add a couple of squirts of liquid dish washing detergent, and mix them together. Pour the 15% H<sub>2</sub>O<sub>2</sub> into the other cylinder and add a similar amount of detergent. Place these containers on the two shallow pans to catch the bubbles that will be produced in the next step. Have a volunteer add the concentrated KI solution (half-full container) to the concentrated H<sub>2</sub>O<sub>2</sub> cylinder, while at the same time having another volunteer add the dilute (full) container of KI into the 15% H<sub>2</sub>O<sub>2</sub> (try writing out the balanced chemical equation or have the class try to balance it). The O<sub>2</sub> produced causes zillions of bubbles to form from the dish washing liquid. This causes a column of very fine bubbles to rise out of the container and spill into the catch pan. Steam will also be produced from the exothermic nature of the reaction.

There will be a dramatic difference in reaction rates for the two cylinders. For the more dilute reaction, you diluted each reactant by a factor of 2 and then increasing the overall volume when mixing them (causing an additional dilution effect). The rate determining step is bimolecular so the reaction for the diluted solutions should go (0.5; relative concentration  $H_2O_2$ ) × (0.5; relative concentration KI) × (0.8 dilution effect from mixing of solutions) = 0.2 relative rate, or 5 times slower than the concentrated solutions. Discuss this with the class along with a simple rate law: rate =  $k[H_2O_2][KI]$ . This clearly demonstrates the effect of concentration on reaction rate. Discuss how a catalyst speeds up a chemical reaction by lowering the activation barrier for that reaction. Discuss how your body has lots of bio-catalysts (enzymes) that speed up many of the too slow metabolic reactions to keep you alive. Discuss how concentration affects the rate of chemical reactions, especially bimolecular rxns like iodide and H<sub>2</sub>O<sub>2</sub>.

**Oscillating Iodine Reaction:** The homemade "kit" from us will contain 3 bottles with the solutions of chemicals that you need to mix together to start the reaction. Add the solutions labeled **A**, **B** & **C** relatively quickly (order is not important) to the beaker or container provided. Swirl the contents to mix them up. The oscillating reaction should start in about 30 seconds and changes colors about 10-15 times.

Use the reaction scheme shown to the right to discuss how the reaction oscillates between  $IO_3^-$  (iodate anion, colorless),  $I^-$  (iodide, colorless),  $I_3^-$  (triiodide, yellow), and  $I_2$ , which forms a deep blue-purple complex with starch.  $Mn^{2+}$  initially reduces the  $IO_3^-$  to HOI. Malonic acid then acts as a reducing agent to reform  $Mn^{2+}$  and iodide anions.  $CO_2$  and formic acid are the products from the oxidation of the malonic acid. The  $H_2O_2$  then takes over as an oxidizing agent to produce  $I_3^-$ ,  $I_2$ , and eventually  $IO_3^-$ .

The key in this reaction is that  $H_2O_2$  only slowly directly reacts with malonic acid and they both react more rapidly with iodate/iodine/triiodide anions (with help from the  $Mn^{+2}$  which acts as a catalyst). This keeps the reaction oscillating until you run out of  $H_2O_2$  or malonic acid. The reaction usually ends up as a deep blue-brown solution indicating that the  $H_2O_2$  is used up first.



It is instructive to have the class count the number of color changes and keep track of the time of each color (organize them in teams to do this). As the concentration of the reactants decreases the reaction goes progressively more slowly as predicted from kinetics.