How to use ThermoBounce to understand chemical kinetics and equilibria

Introduction

Many students of chemical thermodynamics struggle to understand the equations showing how equilibrium constants are affected by changes in entropy, enthalpy and temperature. ThermoBounce was designed to provide a model that helps relate these concepts to an easy-to-grasp dynamic visual experience. In ThermoBounce we depict a population of molecules that can exist in two alternative states -- designated <u>reactant</u> molecules or <u>product</u> molecules – and that can flip between these two states. The model applies most closely to chemical reactions in which a single molecule can flip between two shapes or configurations (isomerization), or between two phases (like solid vs liquid).

ThermoBounce envisions a starting condition in which all the molecules are reactant molecules, but have the potential to turn into product molecules. In ThermoBounce the molecules are represented as balls bouncing against the walls of two adjacent rooms, with a transparent (invisible) wall facing the viewer, and an open window between the two rooms. The balls representing reactant molecules are in the left-hand room, while the balls representing product molecules are in the right-hand room. If a ball crosses through the window from the reactant room into the product room this means it has been converted to a product, and its color changes from brown to green; it may change back to brown if it bounces back into the reactant room. The reaction often reaches a state where the rate of reactant balls turning into product balls is the same as the number of product balls turning back into reactant balls; that is, the reaction has come to equilibrium. In that situation, the ratio of product to reactant balls reflects the equilibrium constant.

The floor heights of the left and right rooms represent the chemical potential energy of the reactants and products, respectively. If the floor of the left room is higher than the floor of the right room, the conversion of reactants to products is exothermic (releases energy); if it is lower, the reaction is endothermic. The areas of the floors of the two rooms represent the entropy of the reactant and product molecules; a larger room means greater entropy (larger space of possible configurations).

The rate of the chemical conversions depends on the width of the open window between the two rooms, corresponding to the entropy of activation; a narrower window slows the reaction rate. The rate can also be slowed if the bottom of the window opening is so high that very few balls have enough energy to reach this height and cross from one room to the other.

What makes ThermoBounce fun to explore is that users can modify many parameters and observe how these changes affect the reaction. Before trying modifications, let's watch a ThermoBounce reaction running the under the default conditions. First open the program by using the ThermoBounce URL: (https://web.cs.uc-davis.edu/~max/kinetics.html). This should bring you to the screen shown in Fig. 1, which depicts the first of three states, each identified by the small colored square at the bottom right corner.
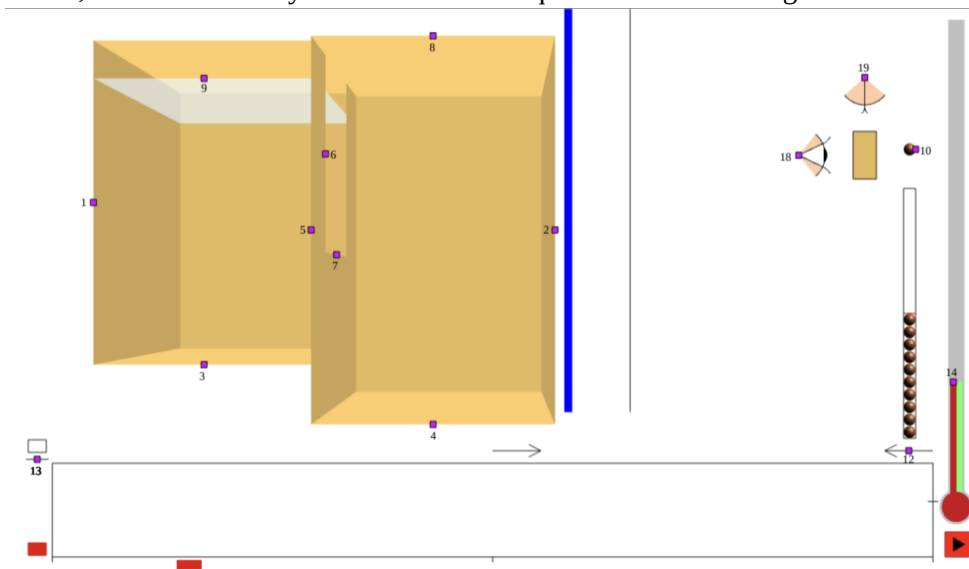
Figure 1. State 1 (red square state)

In the state shown – State 1 (initiation), with a red button – you can adjust several <u>experimental</u> variables and <u>viewing</u> variables; but for your first run, leave all variables at their default values and click on the red square to advance to the next state. State 2 allows adjustment of two experimental variables (the temperature and number of balls) and has a yellow square button in the lower right corner. Click on this yellow button: it will turn green (state 3) and get the program running with the balls bouncing. Watch what happens as the program runs its course!

As the balls bounced between the rooms, the graph below the rooms uses a red line to trace the fraction of total balls in the product room; this fraction is initially zero, but increases during the reaction, leveling off at roughly 0.60 or 60%. Below the graph, the parameters used in this experiment are recorded underneath a rectangle with a matching red color. You can change each of these experimental parameters (as described below) before each subsequent experiment, so you can see how they influence the progress of the reaction. Each new experiment will add a different color tracing, with the parameters for each experiment recorded in a new column below the graphic tracing. Also recorded in this column is the final fraction of balls in the product room.

Notice some other features in the ThermoBounce display.

- To the right of the rooms is a graphic indicating how fast the balls are bouncing at each moment in the experimental run. In the histogram, the height of the blue bars shows the number of molecules in each of 40 velocity magnitude bins, with increasing velocity to the right; and the pink curve shows the theoretical (Maxwell-Boltzmann) distribution of velocities for the same average kinetic energy per ball, which the blue bars approximate.
- Above right from the histogram is a view selection tool represented by an open eye (the viewer) looking at a tan rectangle (the two rooms). If you want to step back from the rooms so that you can see balls bouncing so high that they are above your current view of the room, click on the magenta square button and drag it to the left to move it farther from the tan rectangle representing the rooms; this allows you to see the upper reaches of the room. If you would like a view from above the room, click on the magenta handle of the closed eye above the room; this eye now opens, and you can now see two rooms from above the product room. You can then move the magenta square up or down to move farther away from or closer to the floor.

Altering parameters to test their effects on the reaction.

The parameters you can change depend on which of four states of the program you are in. States 1, 2 and 3 correspond to the red, yellow and green state square buttons in the lower right corner. State 4 corresponds to the green state after a run has been completed.

To learn how you can alter various experimental parameters, click on the green state button to return to the initial view (state 1, with a red state square in the lower right). In this state you can click and drag on magenta square handle buttons 1 through 9 to move the boundaries of the rooms and the dimensions of the window between them. (See Table 1 below.)

Table 1. Key to the mouse interaction buttons.

Label	Figure	Explanation
1	1	Left wall: adjusts both length and depth of left reactants room
2	1	Right wall: adjusts both length and depth of right products room
3	1	Left floor: adjusts floor height of left room, *i. e.* reactant chemical potential
4	1	Right floor: adjusts floor height of right room, *i. e.* product chemical potential
5	1	Door wall: adjusts position of separating wall, without changing other walls
6	1	Door width: adjusts width of window, *i. e.* activation entropy
7	1	Door height: adjusts height of window bottom, *i. e.* activation energy
8	1	Ceiling height when finite; toggle between finite or infinite by typing 'i'
9	1	Molecule height: caps height and thus energy of initial sphere placements
10	1	Sphere radius: adjusts sphere radius
11	4	Expand graph: magnifies time scale on reaction progress graph
12	1, 3, 4	Compress graph: compresses time scale on reaction progress graph
13	1, 2, 3	Button bar: lower to push buttons down, showing fewer colored graph curves
14	2, 3, 4	Temperature: sets desired temperature; may be dragged at any time
15	2	Sphere stack top: adjusts the number of molecules in the simulation
16	3, 4	Graph buttons: toggle on and off the drawing of the reaction progress graphs
17	3, 4	Prior temperatures: click to set desired temperature to a previous graph's value
18	1	Front view icon: click for front view, drag to move viewpoint closer or farther
19	1	Top view icon: click for top view, drag to move viewpoint closer or farther

For example, to lower the floor of the reactant room, representing the enthalpy of the reactant state, click on magenta button #3 and drag it down; notice that as you move, the table below the graphic shows a decrease in the reactant enthalpy. Simultaneously the activation enthalpy – represented by the difference between the height of the reactant floor and the bottom of the window between the two rooms – increases. This means that only the most energetic balls that bounce high enough to scale the windowsill can cross through the window. You can alter the height and width of the window by clicking and dragging buttons 6 and 7. Explore how you can alter the floor areas of the two rooms (and their entropies as shown in the table) by changing the floor heights of the rooms (buttons 3 and 4) and also their widths (the buttons on the vertical edges of walls – buttons 1, 2, and 5).

Another important thermodynamic parameter that can be altered is the temperature of the reaction. Higher temperature means that the molecules have more energy, which in ThermoBounce means that the balls are moving faster and thus bouncing higher on average. The desired temperature is shown by the red bar in the thermometer at the right of the visualization, and can be adjusted by clicking and dragging the temperature button at the top of that bar. This adjustment can be made in any state of the program, even in state 3, when the animation is runningn The light green bar to the right shows the actual average temperature of the balls in the simulation. The actual temperature may lag the specified temperature because energy of the balls changes only when a ball collides with a room wall or floor, and changes in a way that will incrementally move the room's average temperature to the specified desired one, much as the temperature of a container would influence the temperature of an enclosed gas. The thermometer setting at the start of each simulation run is marked by the short horizontal bar to the left of the thermometer; the color of the bar corresponds to the color of that simulation. This may be useful if you want to repeat an earlier simulation at the same constant temperature, perhaps changing another parameter. You can copy a previous experiment's temperature to the current experiment by clicking the bar with a segment of the appropriate color. After the new simulation starts, the bar will have a segment colored by the graph color of the new simulation.

Another experimental parameter that can be adjusted in state 1 (red) is the size of the balls. To adjust ball size, click and drag button 10 to the right of the eyeball view icons. Large sized balls may be easier to see, but will limit the number of balls that can fit in the reactant room to run the simulation.
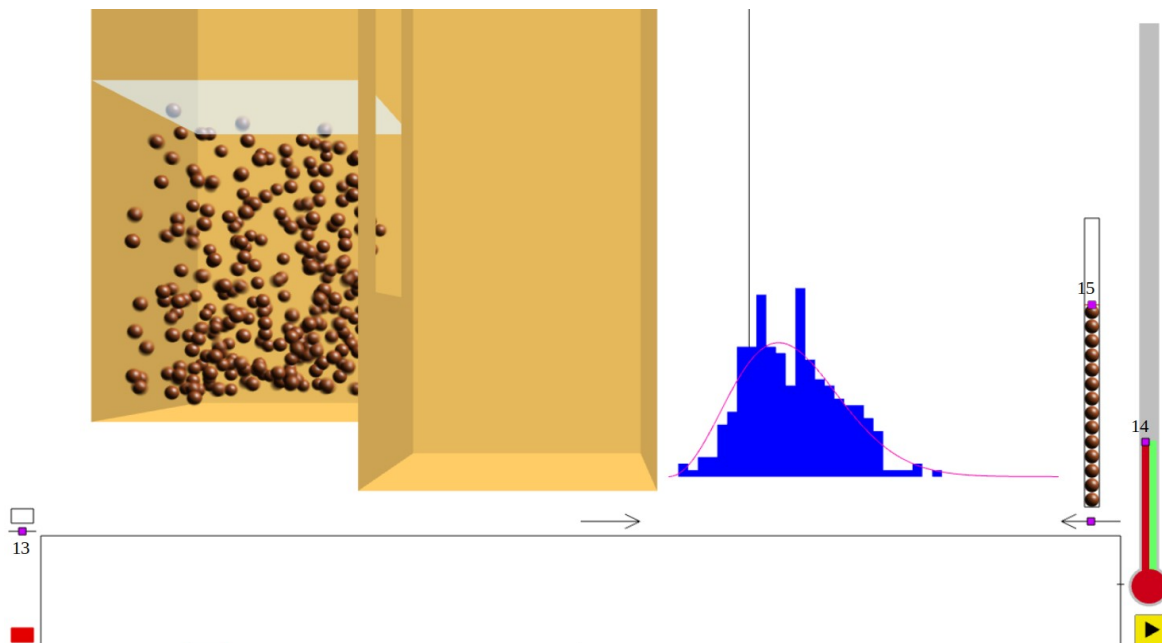

Figure 2. State 2 (yellow state square)

Now click the red state square to move to state 2. In this state you can adjust the number of balls in the simulation. This is accomplished by moving the magenta button at the top of the stack of balls in the thin vertical box below the ball size adjustment icon. Move the button up to increase the number of balls, down to decrease. Now click the yellow state square to move to state 3 and start the simulation.

To stop the simulation either when it is running, or when it is paused because the graph is complete, click the (now green) state button at the bottom right returning the simulation to state 1, so you can start another run. Up to six reaction progress graph curves may be drawn, each with a different color, as shown in Figure 4, by clicking the red state button again.
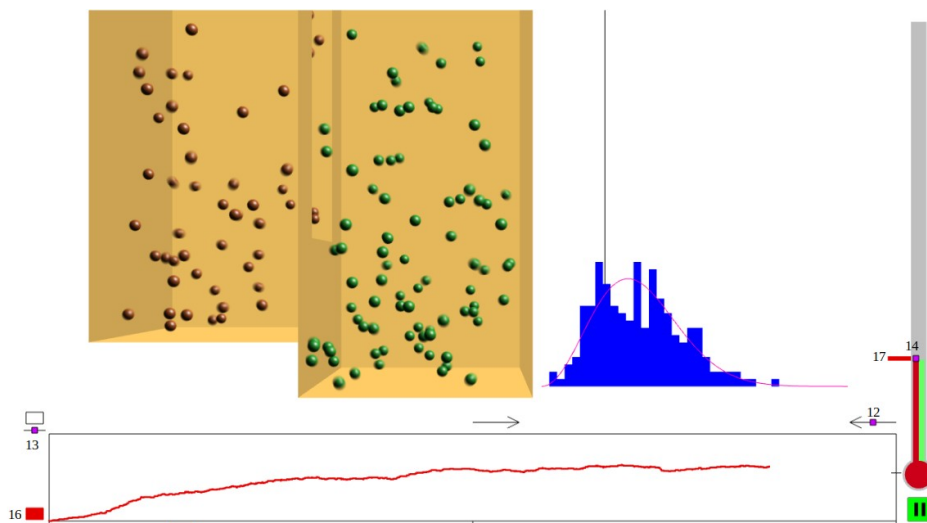

Figure 3. State 3 (green state square)

If more than six simulations are started, the data and graph of the least recent one will be deleted, and its color will be reused for the new one. As shown in Figure 4, six reaction progress graph curves may overlap each other, leading to a cluttered display.
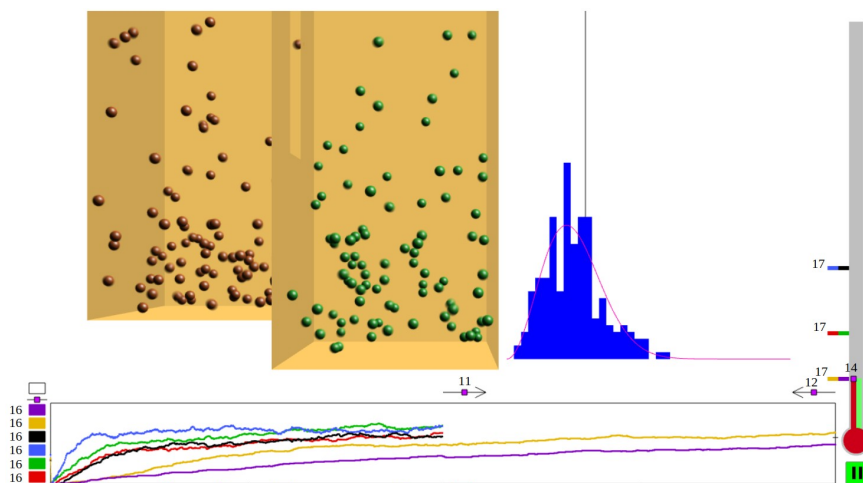

Figure 4. State 3 after 6 simulations, and progress graph compression.

There is a stack of colored rectangular bars to left of the graph, with the most recent color at the top, which may be clicked to toggle off and on the graph curve of the corresponding color. Alternatively, the handle with the label 13 in figure 3 on the black line at the top of the stack may be clicked and dragged downwards, which pushes all the bars down. When bars disappear off the bottom, the corresponding graphs curves are blanked out. They reappear in order if that handle is clicked and is raised. This is an easier way to display only the most re-cent few graphs.

Initially each pixel on the reaction progress graph is the average of two consecutive frames' reaction prod-ucts fractions, so the 1201 pixel width of the graph allows for 2402 frames, and then the simulation pauses. Sometimes this is not enough time for the reaction to go to its equilibrium state. Therefore, the graph can be compressed by clicking the magenta square called a "handle" labeled 12 in Figure 3 on the left pointing com-pression arrow above the graph. This compresses the graph or graphs by a factor of 2, as shown in Figure 4, with 3 intermediate time tick marks on the horizontal axis, instead of 1, and the simulation continues, and draws the rest of the graph until it fills up the newly created space, and then pauses again. Handle 12 can be clicked a total of 3 times, allowing a compression by a factor of 8, and then handle 12 disappears. But whenever there is any compression, handle 11 appears on the right pointing arrow above the center of the graph, and can be used to ex-pand the graphs away from time step 0.

In Figure 4, the left-hand reactant room has been made smaller, and its floor raised, thus favoring the prod-uct by both entropy and energy. The horizontal line across the right-hand border of the progress graph represents the equilibrium product fraction at very high temperature, when only entropy is significant, and is set to the ratio of the floor area of the right-hand room to the total floor area of both rooms. After the first four experiments, the reaction progress graph was compressed, so that the first four curves extend only halfway across it, and the last two experiments ran twice as long, extending to the right-hand end of the graph, for 4804 simulation steps. The state button is still green, and it needs to be clicked to turn it red in order to start a new simulation.

There are also several adjustments you can make with the keyboard or mouse. If you type the character 't', you can toggle back and forth between the normal side view, with the wall closest to the viewer made transpar-ent, and a **t**op view of the rooms with their ceilings made transparent. If you type 'i' you can toggle the ceiling height between finite (and adjustable with handle 8), and **i**nfinite. When the ceiling height is finite, the entropy of a room is represented by its volume rather than its floor area. If you type 'r' you can toggle from **r**andom ini-tial positions to initial positions in a face-centered-cubic crystal. If you type 's' you can **s**uppress the ball-ball collisions, saving computation time if the number of balls is large, since after a ball collides with anything, the

program must check its new potential collisions with all the other balls, to see which potential next collision would happen first. The balls are drawn in back-to-front order, so that motion-blur caused transparency effects are possible. So when collisions are suppressed, the drawing order may suddenly change, causing one ball to pop in front of another. If you type 'o' you can toggle back and forth between an **o**rthogonal view and a perspective view. If you type 'v' you can stop the simulation, and if you type 'v' again, you can restart the simulation. While the simulation is stopped, you can advance it by one frame by typing 'g'. If you type 'b' the current simulation will go **b**ack to the state where the state where the state button is red. This is useful when the state button is yellow and you want to change the geometry, or when the state button is green and you want to see the same simulation run again with different initial random positions and velocities. If you type 'u' the initial distribution of vertical positions will be **u**niform, instead of decreasing exponentially with height.

When you change the temperature while a simulation is running, the change or jump in temperature may be indicated by colored arrows on the reaction progress graph, as shown in figure 5. These colored arrows are not initially shown for any of the experiments with temperature jumps, but if you type 'j' you can display the ones for the current experiment, if any, and if you type 'j' again those for all experiments are shown. Typing 'j' a third time will again show none of them, and subsequent such typing will cycle through these three alternatives.

If you drag the mouse with the center button clicked, you can translate the image of the rooms across the screen. If you turn the scroll bar you can move the rooms closer to or farther from your viewpoint. You can also drag the eye icons as described in the second bullet entry at the end of the previous section to move the viewpoint. If you drag the mouse with the right button depressed, you can rotate the rooms and balls in 3D. Initially the rooms rotate only around the vertical **y** axis but if you type 'y' you can change to a more flexible interface that allows arbitrary rotations. If you want to get back to the original view before any such mouse dragging or scrolling, you can type 'f'. You can remove the **e**ye icons by typing 'e' and put them back by typing 'e' again.

There are several lines below the display showing the current values of parameters like enthalpy determined by the room geometry, and other parameters like temperature. In order to adjust these parameters for an efficient comparison of their effects, it is useful to be able to go back to an earlier set, and then change one or two to see a new simulation. This can be done while the state button on the lower right is red or yellow and the new simulation has not yet started, by clicking the colored button in the stack of buttons on the lower left corresponding the desired earlier simulation, while holding down the control key. This will change the initial parameters for the new simulation to those of the earlier one. Then to edit one or more of these parameters, control-click the white button above the other colored ones. Clicking a colored button while pressing the control key while the state button is green and the simulation is running will halt the simulation and change the display the room geometry used to produce the curve of that color without changing that of the current simulation, so they can be compared at any time. To display the geometry for the current simulation again and resume that simulation, just control-click the white button above the other colored ones.

When copying parameters by control-clicking a colored button, any temperature jumps will also be copied to the new experiment. If you only want to copy the geometric parameters and initial temperature, without copying these temperature jumps, type the letter 'd', for "**d**o not copy", before control clicking. If you later want to copy the temperature jumps, type 'd' again to turn on this copying. With the copying turned on, you can copy the temperature change schedule from one simulation, and then by typing 'd' to turn it off, you can copy the geometric parameters (but not the initial temperature) from another one into the same new experiment. (If you have not copied any temperature jumps, then the initial temperature is also copied.)

A black vertical line on the Maxwell-Boltzmann graph shows the velocity which a ball bouncing from the floor of the reactant room on the left would need to reach the height of the window between the two rooms and potentially undergo a reaction. The position of this line varies when the handles labeled 3 and 7 are moved to change the height of the floor of the reactant room or of the bottom of the window, respectively.

In order to facilitate comparison of the parameters used for the six most recent simulations, they are printed in columns under the graphs, as shown in figure 5. The color of the graph for each column is indicated by the text title above it, as well as by the colored rectangle farther above it. Unlike the stack of rectangles on the left of the graphs, the colors for these columns remain the same, so that the numbers in the columns do not jump around. The column whose parameters are currently being edited or run corresponds to the topmost color in the stack of rectangles on the left and is indicated by a longer colored rectangle at the top of its column, in this case the black one. The current temperature in the next to the last row can change if the handle at the top of the red

bar in the thermometer is used to change the temperature while the simulation is running, and when it is finished, that becomes the final temperature of the current experiment, and the initial temperature of the next experiment. This row and the product fraction row are continuously updated as the simulation runs.

The last "Keyboard interaction" column of the table does not correspond to any specific experiment, and instead lists some of the keyboard letter keys discussed above, and the current state of the option that the key controls. A more complete list is in the companion document at https://web.cs.ucdavis.edu/~max/Key_meaning.pdf .

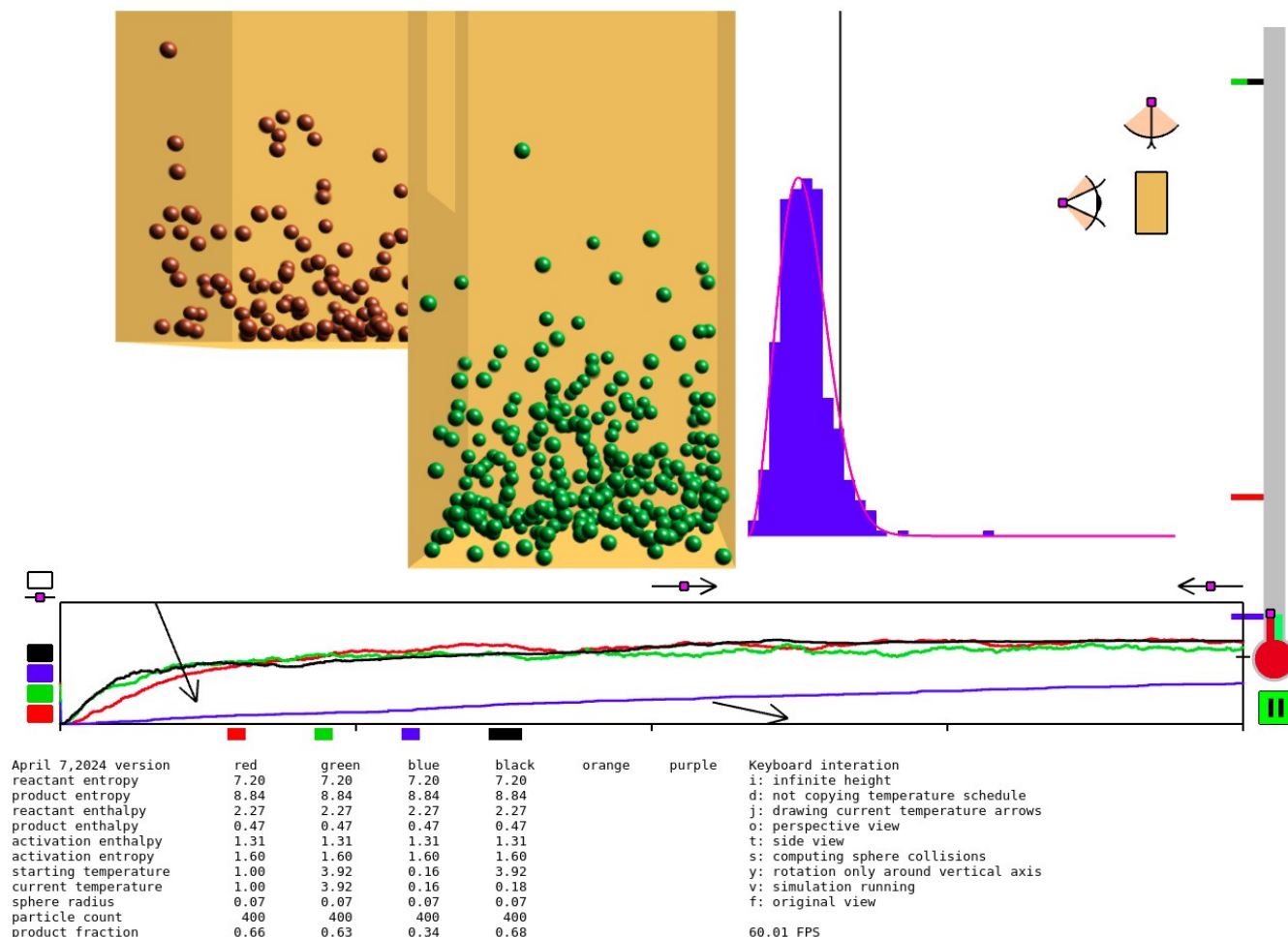| April 7,2024 version	red	green	blue	black	orange	purple	Keyboard interation
reactant entropy	7.20	7.20	7.20	7.20			i: infinite height
product entropy	8.84	8.84	8.84	8.84			d: not copying temperature schedule
reactant enthalpy	2.27	2.27	2.27	2.27			j: drawing current temperature arrows
product enthalpy	0.47	0.47	0.47	0.47			o: perspective view
activation enthalpy	1.31	1.31	1.31	1.31			t: side view
activation entropy	1.60	1.60	1.60	1.60			s: computing sphere collisions
starting temperature	1.00	3.92	0.16	3.92			y: rotation only around vertical axis
current temperature	1.00	3.92	0.16	0.18			v: simulation running
sphere radius	0.07	0.07	0.07	0.07			f: original view
particle count	400	400	400	400			
product fraction	0.66	0.63	0.34	0.68			60.01 FPS

Figure 5. State of the parameters when the experiment for the black graph has finished.

Sometimes the simulation gets into an infinite loop of collisions within one frame and times out, and a window pops up saying so. If you click OK on that window, you can restart the simulation on the same color graph, with the same parameters and new random positions and velocities.

Tutorial Appendix

A) Without moving any of the handles, try clicking the state button twice to begin the simulation, and let it run until it stops when the reaction progress curve reaches the right hand side of the graph. Note the height at the last point, indicating the product fraction. The height of the top of the box around the graph represents the product fraction 1, meaning that all the balls are in the right hand room, and all the reactants have turned to products.

B) Since the temperature is proportional to the average kinetic energy of the balls, raising the temperature on the thermometer will increase the heights of the bars at the right, for bins with higher velocities, and decrease the heights of bars on the left, and the peak of the pink curve for the Maxwell-Boltzmann distribution will shift

to the right. Similarly, lowering the temperature will move the peak to the left, and make it higher, because the area under the curve (and the total areas of all the blue bars) is 1, representing the total number of balls. Try lowering the temperature to 0.20 by clicking with the left mouse button on the pink handle at the top of the red bar in the thermometer, and dragging the mouse cursor downwards while holding down that mouse button. You will be changing the parameters for the green curve, which is the color of the next reaction progress curve to be drawn. You can see the temperature you are setting as both the starting temperature and the current temperature in the second column of the table at the bottom of the screen, labeled with a green box (wider than the red box to its left, to indicate the column of parameters you are currently editing), so you can look at these numbers as you move the mouse in order to reach exactly 0.20. Then click the state button twice to start the simulation, and let it run until it stops when the reaction progress curve reaches the right hand side of the graph. At a lower temperature, fewer of the balls have enough upward velocity to reach the height of the window, so the reaction rate is slower.

C) At this slower rate, the reaction has not progressed to equilibrium in the time the curve reaches the end of the graph; the curve is still rising. So click the handle on the left-pointing arrow above the right end of the reaction progress graph box. This will squeeze the time scale to the left by a factor of 1/2, as indicated by the closer spacing of the time ticks at the bottom of the graph. The simulation will now proceed until the green curve is twice as long as the squeezed red curve. When the simulation stops, you can click that handle a second time, and the simulation will continue until the green curve is four times as long as the red one. By now, the green curve has flattened out, and probably reached a height (product fraction) slightly above that reached by the red curve. You can click the handle on the left pointing arrow a total of 3 times, extending the simulation time by a factor of 8, and then that handle disappears. As long as the graph is compressed, there is a handle on the right pointing arrow to the left of the left pointing one, which you can use to expand the graph back to its original scale.

D) Now start a new simulation, by increasing the temperature to the maximum value on the thermometer, which is 3.92. At the resulting high velocities, the balls are drawn with motion blur, even in the non-moving initial frame. Increase the number of balls to 400, by raising the handle at the top of the stack of balls to the left of the thermometer. This will decrease the random up and down fluctuations in the reaction product graph by a factor of the square root of two. The balls will be moving with so much energy that most of them will be out of view above the top of the screen. They will now have no trouble reaching a height above the bottom of the window, and will easily pass through the window, in both the forward reaction direction (left to right) and reverse directions. At high temperatures, the enthaply difference between the reactants and products (the difference of the floor heights of the two rooms) has very little effect, and the final equilibrium product fraction is determined by the entropies of the reactants and products, corresponding to the floor areas of the two rooms: the product fraction is the ratio of the floor area of the product room to the total floor area of both rooms, since if the balls can pass freely between the two rooms, there will be a constant expected number of them per unit floor area. The high-temperature-limit product fraction is represented by the black tick at the right end of the graph box, and the curve for any simulation at high temperatures should end up near this black tick, but will usually not stop there exactly, due to the random up and down fluctuations of the curve.

E) It might be easier to visualize and understand the effect of the entropy with a finite ceiling for the two rooms. You can make the ceiling height finite by typing the 'i' key. Then an extra handle controlling the ceiling height appears, labeled 8 in figure 1. The analog of the entropies of the reactants and products switches from the areas of the floors of their respective rooms to the volumes of the rooms, and you can see the entropy numbers suddenly change, and the black tick mark on the right side of the graph slightly shift. If you move the handles for the ceiling or walls of the rooms, the entropy numbers change continuously. It may be easier to understand the entropy analogy with a finite ceiling. The balls start in the left hand reactant room, and the product room is empty. The elastic collisions of "hard" balls are a model for the dynamics of a gas. So at high temperature, we initially have a gas at high pressure in reactant room, and a vacuum in the product room. The gas can freely flow through the window, so the pressure will equalize in the rooms, and the number balls in each room will be proportional to the room's volume (except for the small statistical fluctuations).

(F) Suppose your goal is to have the largest possible product fraction at the end of a specific time interval, for example, the 2402 time steps in the initial graph, without changing the room geometry. We have seen that a higher temperature makes the initial slope of the graph lager, and it reaches its equilibrium value and flattens out more quickly. But a lower temperature changes the equilibrium value, since the difference in reactant and product enthalpies has more effect. The temperature can be changed during the simulation, by moving the handle at

the top of the red bar in the thermometer. In a finite-ceiling room, raise the handle at the top of the stack of balls to increase the particle count to its maximum value, 400 (for a smoother graph), and raise the handle on the temperature to increase it to its maximum value, 3.92 (for a faster movement towards the high temperature equilibrium). The product graph should end up at or near the black tick on the right of the graph, indicating the ratio of the volume of the right room is to the total volume of both rooms. Then click the state button three times to start a new simulation with the same parameters, but this time, while the simulation is progressing, use the handle on the red thermometer bar to lower the temperature to reach about 0.20 before the simulation is half over. This sets the specified temperature, and causes balls to gain or lose energy as they bounce on the walls, to make the temperature approach the specified temperature in both rooms. The green bar on the thermometer indicates the actual temperature computed from the actual particle energies, and may lag the specified temperature a little if there have not been enough collisions with the walls. Since the enthalpy difference has more of an effect at lower temperatures, the graph should now end up above the black tick mark for the high temperature limit, and reach that level more quickly than if the temperature was initially 0.2 as in case (C) above. Note that the current temperature row is the column of parameters at the end of the simulation is the last temperature you have specified, and will become the default initial temperature of the next simulation you start. The initial temperatures of the other curves are shown as colored bars (or colored pieces of bars) of different heights at the left of the thermometer, and if you want to specify a new initial temperature to be the same as on a previous curve, just click the corresponding bar.

(G) Another way to speed up the reaction rate is to make the window between the rooms wider, by clicking and moving the handle at the side edge of the window, labeled 6 in Figure 1. This increases the number of trajectories by which a ball can pass through the window. It is analogous to increasing the entropy of activation, which increases the number of transition states by which the reaction can progress.

(H) A related way of increasing the window size it by lowering its bottom, by clicking and lowering the pink handle labeled 7 in Figure 1. But the main effect of this is to lower the energy that a ball needs to get from the floor to a height higher that the bottom of the window, so it is analogous to the activation enthalpy. Lowering the window bottom height has the same effect on the reaction rate as increasing the temperature, as in cases B) and D) above.

(I) Another way to make more balls end up in the product room is to increase its size, as compared to the size of the reaction room. You can do this by clicking and moving the handle labeled 5 in figure 1 to the left, which moves the whole wall separating the two rooms to the left, making the left room smaller and the right room larger. This will change the entropies of the two rooms, and the reaction favors the room with larger entropy, especially at higher temperature. There is another way to change the size of a room, by clicking a handle on the room wall opposite the one with the window separating the rooms, which is labeled 1 in figure 1 for the left room, and 2 for the right room. Moving these handles also changes the front-to-back depth dimension of the room, making the change in the floor area (or volume) more pronounced.

(J) A final way to increase the product fraction is to make the difference between the two rooms' floor heights larger, for example, by lowering the floor of the right room using the handle labeled 4. This makes the reaction more exothermic, and the balls are then more likely to remain in the right room once they get there, especially at lower temperatures. Instead or in addition, you could raise the floor level of the left room by clicking and raising the square labeled 3.