

Studying the Equilibrium of a Water System

In this experiment you will be using a simulation to measure the vapor pressure of water in a closed system at different temperatures.

Download the simulation at: <http://sites.google.com/site/carollundssimulation/site/>

The following chemical processes and properties will be studied:

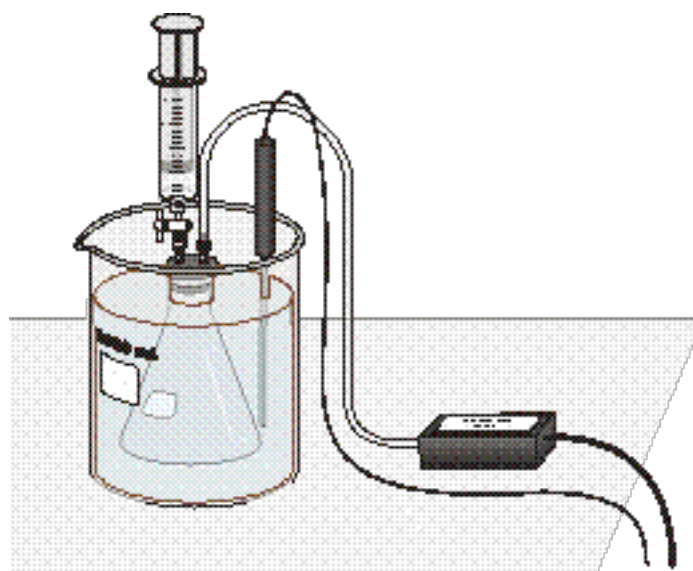
Rate of this reaction at different temperatures: $\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{O}_{(v)}$

Equilibrium properties of this reaction at different temperatures: $\text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_2\text{O}_{(v)}$

In this Simulation you will measure vapor pressure, molarity, time, and temperature of a closed system containing liquid water and water vapor. Using the equilibrium vapor pressure of water at different temperatures you will be able to calculate the molarity of the water vapor. With the equilibrium vapor pressure and equilibrium molarity at a range of temperatures you will be able to calculate the equilibrium constants K_p and K_c for the reaction shown above at different temperatures. You will also create a graph of $\ln P$ vs $1/T(K)$ and from the slope of the line ($-\Delta H/R$) you will determine the enthalpy of vaporization for water.

The simulation assumes the following experimental conditions for generating the data: a flask with a volume equal to 1.0 Liters, a temperature range in Celsius from 0°C to 100°C , a value for $R = 8.314 \text{ kPa}\cdot\text{L}/\text{mol}\cdot\text{K}$, and a surface area of liquid water in the system of 1dm^2 .

The simulation is based on the experimental system shown in the diagram below:



The experimental procedure that the simulation is modeled after includes the following steps:

1. Set the temperature of the water bath at 20°C and use a temperature probe to monitor the temperature.
2. Secure the top of the flask with a pressure sensor attached to a rubber stopper.
3. Place the flask setup in the water bath and wait for the temperature of the equipment to equilibrate.
4. Measure the initial room pressure in the flask and add a small (10 ml) volume of H₂O(l) from the syringe.
5. Measure the change in Pressure of water vapor in the flask with time until the pressure readings become constant.
6. Maintain a constant temperature of the flask, water, and water vapor during the experiment.
7. Repeat the experiment at increasing temperatures (30°C, 40°C, and 60°C) by adding hot water to the water bath.

How to use the Simulation to model the above experiment:

1. When you open the simulation you will see a window with two graphs and a number of buttons and data windows.
2. Each time you hit “Play” the simulation will run for 101 seconds and collect vapor pressure values at 1second intervals for 4 different temperatures (20°C, 30°C, 40°C, and 60°C).
3. You can “Pause” the simulation at any time during this time frame, and you can hit “Reset” to run the simulation again.
4. The “Step” button will allow you to increase in time increments of 1 second.

5. By clicking on the “showTank” box you will open a new window with a series of “closed tanks” containing liquid water at four different temperatures and the increase of water vapor until equilibrium is reached.
6. By clicking on the “showEquipment” box you will open a window with the image of the equipment shown above, that you could use in the laboratory to collect pressure and temperature data for water or other liquids, similar to the data presented in this simulation.
7. Finally, by clicking on the “PvTgraph” box you will open a window, which displays a graph and two data windows. You can enter any value for temperature from 0°C to 100°C and a value for the vapor pressure of water will appear in the pressure window and a data point will appear on the graph.

Data Collection and Analysis:

1. Run the simulation (click on the “showTank” box before hitting “Play”) and collect pressure and time data at four different temperatures.
2. Answer the following questions by looking at the pressure time data:
 - a. Describe what is happening in the system to produce the change in vapor pressure from time = 0 seconds to time = 100 seconds.
 - b. What processes occur to cause the change in vapor pressure to become constant?
 - c. Write rate law expressions for the forward and reverse reactions; label the rate constants with the name of the process occurring.
 - d. What is equal in the system at the end of the experiment?
 - e. What is not equal in the system at the end of the experiment?
 - f. Rearrange the rate law expressions to represent the equilibrium expression for the phase change.
 - g. Write the equilibrium expression in terms of the vapor pressure of water at each temperature.
 - h. What happens to the value of K_p as the temperature changes?
 - i. Calculate the number of moles of water vapor at each temperature. Since the total volume used is 1.0L the moles calculated is equal to the molarity. Calculate K_c for the equilibrium system. Which concentration is very close to constant? Does the value for K_c also change with temperature?
 - j. How do the two rate constants compare to each other? Which is greater and which is smaller? Identify which rate constant is associated with the endothermic reaction and which is associated with the exothermic reaction.
 - k. The value of the rate constant depends on the Activation Energy of the reaction and the temperature in the following way $k = e^{-E_a/RT}$. Which activation energy must be greater the activation energy for evaporation or the activation energy for condensation? Explain.

3. Run the simulation again. Compare the equilibrium vapor pressures at the four temperatures. Using these values try to predict the mathematical relationship between vapor pressure and temperature. Explain your reasoning.
4. Open the window for the Pressure vs. Temperature graph. Enter temperature values in 10°C increments and record the vapor pressure that corresponds to each temperature.
5. Look at the shape of the graph and compare the shape to the mathematical relationship you predicted in question 3.
6. Using Graphical Analysis, prepare a graph of $\ln P$ vs. $1/T$ (in Kelvin). Using the Clausius–Clayperon equation: $\ln P = -\Delta H/R (1/T) + C$, where Pressure is in units of kPa and T is in units of Kelvin, and R is 8.314, determine a value for the enthalpy of vaporization of water. Using your table of Thermochemical values calculate the value for the enthalpy of vaporization from the tabulated values. Why are the two values different? Write a thermochemical equation for the phase change measured in this experiment. Which direction represents the endothermic reaction and which direction (evaporation or condensation) represents the exothermic reaction?
7. Explain the reason for the differences in molarity of $H_2O_{(l)}$ at the four temperatures measured. Hint: write units for molarity of water and describe what properties of water you would need to know to calculate the molarity of water at these four temperatures. Which of these properties is likely to change with changing temperature?
8. Run the simulation again and record the initial values for the molarity and vapor pressure for each temperature. Record the equilibrium values for the molarity and vapor pressure. What is the relationship between these values? What happens in the sealed flask to produce these amounts? Compare your calculations for the number of moles of water that changed to a vapor at each temperature to the change in the molarity of the liquid water at each temperature. Do your numbers match?