Le Chatelier's Principle

The Effect of Temperature on Equilibrium

Le Chatelier's Principle states that if a system at equilibrium is subjected to a change of conditions, reactions occur in the system that tend to counteract the imposed change. In other words, the system tends to react in a way that restores the equilibrium. When the imposed stress is an increase or a decrease in pressure, reactions that involve gases are greatly affected. In general, an increase in pressure (a decrease in volume) favors the net reaction that decreases the total number of moles of the gases. A decrease in pressure (an increase in volume) favors the net reaction that increases the total moles of gas.

In this experiment, you will investigate how changes in temperature affect the position of equilibrium in a gaseous reaction. A convenient reaction to use is the equilibrium between two gases: nitrogen dioxide (NO_2) and dinitrogen tetroxide (N_2O_4).

$$\underset{\text{red-brown}}{2\,NO_{2\,(g)}} \quad \leftrightarrow \quad \underset{\text{colorless}}{N_2O_{4\,(g)}}$$

Nitrogen dioxide will be prepared **<u>in the hood</u>** by the following reaction:

$$Cu_{(s)} + 4\,HNO_{3\,(aq)} \rightarrow Cu(NO_3)_{2\,(aq)} + 2\,H_2O_{\,(l)} + 2\,NO_{2\,(g)}$$

NO_2 is an odd electron molecule that does not obey the octet rule. It readily dimerizes to form the colorless N_2O_4 molecule that does obey the octet rule. The NO_2-N_2O_4 equilibrium is established as soon as the NO_2 is produced and it temperature dependent. The gas mixture is collected in a cuvette and the amount of NO_2 gas is determined using a spectrophotometer. Mixtures containing large amounts of NO_2 absorb light strongly over much of the visible range. Mixtures containing more N_2O_4 than NO_2 absorb less light and have a lighter color. One can thus estimate the relative amount of NO_2 in a sample mixture by observing the color of the gas and determine it quantitatively by measuring its absorbance.

In this experiment, you will gradually change the temperature of a mixture of the two gases by placing the gas mixture in hot and cold water. The change in amount of NO_2 in the gaseous mixture will be measured at a wavelength of approximately 500 nm. A graph of absorbance vs. time will illustrate how both increasing and decreasing the temperature of the system affects the amount of NO_2 in the mixture at equilibrium.

Name:___________________________________ Partner:___________________________

PROCEDURE

Set the spectrophotometer to a wavelength of 500 nm. Adjust the % transmittance to zero with no cuvette and to 100% with an **empty cuvette** in the cell compartment. Obtain a second clean cuvette and a yellow No. 1 snap cap that fits tightly on the cuvette. Collect some of the NO_2 gas from the setup in the hood. Quickly put the snap cap on the cuvette and further seal it with a layer of Parafilm.

Put the cuvette in the Spectronic 20 and read its absorbance. The absorbance should initially read 0.50. If it does, record the absorbance and proceed to the cold water step of the experiment. If it does not, the wavelength must be adjusted so that an absorbance of 0.50 is obtained. If the initial absorbance is greater than 0.50, increase the wavelength until the absorbance reads 0.50. If the initial absorbance is less than 0.50, decrease the wavelength until the absorbance reads 0.50**. If the wavelength is changed be sure to readjust the 100 % transmittance with the empty cuvette**. Record the absorbance of the mixture at room temperature and the wavelength used.

Cold Water

Place the cuvette with the NO_2 in a beaker of ice and water for 5 to 6 minutes to cool the gas mixture. Quickly dry the cuvette from the ice water bath and place it in the cell compartment. Take the absorbance readings every 20 seconds from time zero to 4 minutes and then every minute for a minimum of 10 minutes. Continue taking readings until the absorbance values stabilize. Record for a maximum of 14 minutes. You can put the cuvette back into the ice water bath and redo this part if necessary.

Hot Water

Remove the cuvette from the spectrophotometer and place it in a beaker of water at a temperature of between 80-90°C for 5-6 minutes. Quickly dry the cuvette and place it in the cell compartment. Take absorbance readings as above until the absorbance values stabilize or until the 14 minute time is reached.

TAKE THE CUVETTE TO THE HOOD AND REMOVE THE CAP TO VENT THE NO_2 WHEN DONE.

DATA AND CALCULATIONS

Wavelength selected for absorbance measurements _________________ nm

Absorbance at above wavelength at room temperature ____________________

Name:________________________________ **Partner:**____________________

Time Min.	Cold Water Absorbance	Hot Water Absorbance
0.0		
0.33 (20 s)		
0.67 (40 s)		
1.0		
1.33		
1.67		
2.0		
2.33		
2.67		
3		
3.33		
3.67		
4.0		
5.0		
6.0		
7.0		
8.0		
9.0		
10.0		
11.0		
12.0		
13.0		
14.0		

Name:________________________________ Partner:________________________

RESULTS

Plot absorbance vs. time for the hot water experiment and the cold water experiment on the same graph.

1. Which species is favored at high temperatures? Explain your answer.

2. Which species is favored at low temperatures? Explain your answer.

3. Is the $2\ NO_{2\ (g)} \rightleftarrows N_2O_{4\ (g)}$ reaction exothermic or endothermic? Explain your answer.

4. Does your graph show that the system gradually returns to the original gaseous mixture after it has been heated? After it has cooled? If not, what error could have occurred?

Name:________________________________

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Prestudy

Given the following equilibrium:

$$PCl_{5\,(g)} \leftrightarrow PCl_{3\,(g)} + Cl_{2\,(g)};\ \Delta H = +87.9\text{ kJ}$$

1. Are products or reactants favored when the following changes are made to the above equilibrium? Explain your answer in each case.

a. The temperature is decreased.

b. The external pressure on the system is decreased.

c. A small amount of solid is added to the system that reacts only with Cl_2 gas, removing it from the system.

d. Some of the PCl_5 gas escapes from the system.

e. Simultaneously, the temperature is increased and the external pressure is decreased.