

Gaseous Equilibrium of NO₂

Purpose: You will quantify the molar densities of gases in a mixture; you will use those molar densities to calculate the equilibrium constant (K_c) for a chemical reaction involving the gases; and you will study the change in that equilibrium constant with changing temperature.

Measurement background: Last semester we learned about the Beer-Lambert Law, the fact that the concentration of a light-absorbing solute is proportional to the amount of light it absorbs. This law also applies to the molar densities (in mol/L) of colorful gases. For example, nitrogen dioxide (NO₂) gas absorbs light in the ultraviolet-to-blue range of the spectrum resulting in an orange-colored gas—the higher the NO₂ molar density, the more intense the orange color. The Beer-Lambert Law can be expressed as

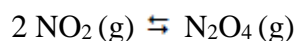
$$A = \epsilon bc$$

in which A is the absorbance (unitless) of a measured sample, ϵ is a property of the measured material called **molar absorptivity** (in L/mol•cm), b is the path length (in cm) through which light travels in the measurement, and c is the molar density (in mol/L) of the measured sample. Therefore, if we know the molar absorptivity of the gas that we're measuring and the path length of our measurement method, then we can use a measured absorbance to calculate molar density. [Hint: rearrange the expression above into an equation for molar density (c).]

Chemical reactions background: You will obtain a sample of nitrogen dioxide gas produced by the reaction of copper metal and nitric acid in a gas generator apparatus located in a hood in the lab. The gas generator is illustrated in the figure on the next page. The chemical reaction is



However, nitrogen dioxide is always in equilibrium with dinitrogen tetroxide (N₂O₄):



So your gas sample is actually a mixture of NO₂ and N₂O₄. Because dinitrogen tetroxide forms from the simple connection of two nitrogen dioxide molecules, N₂O₄ is also called the **dimer** of NO₂. The exact amounts of the two components in this gas mixture depend on the value of the equilibrium constant

$$K_c = [\text{N}_2\text{O}_4]/[\text{NO}_2]^2$$

in which the component amounts—[N₂O₄] and [NO₂]²—are molar densities (in mol/L). The value of K_c for the dimerization equilibrium changes with temperature. Since N₂O₄ is a colorless gas and NO₂ is an orange gas, we expect changes in the value of K_c to result in changes in the color intensity of our gas mixture samples.

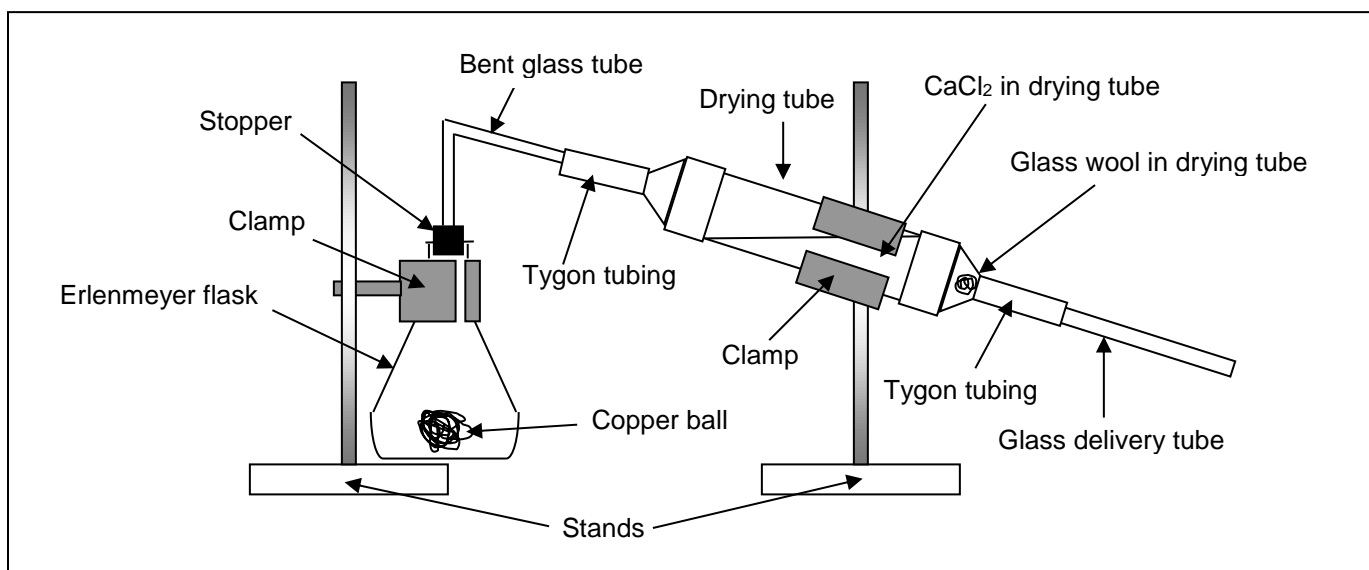


Figure: Gas generator apparatus; orange NO_2 gas forms when copper reacts with nitric acid in the flask, and then the gas passes through a drying tube and is eventually collected in a screw-cap cuvette

Spectrophotometer measurements: Please review the instructions for operating the Spectronic 20 instrument. We will use a screw-cap cuvette containing only air as our blank to set zero absorbance. And we will measure absorbance at a wavelength of 450 nm. (Nitrogen dioxide absorbs 450-nm photons, but dinitrogen tetroxide does not absorb 450-nm photons.)

Obtain: Two screw-cap cuvettes; cuvette rack

Procedure: These are the steps that you will do in the lab. We will work in pairs. And don't forget your eye protection!

PHASE 1: Collect and Measure Your NO_2 Gas Sample

1. Take one screw-cap cuvette—both cuvette and cap—to the hood with the gas generator apparatus. Your instructor and/or lab assistant will provide guidance and instructions for safely filling the cuvette with orange NO_2 gas. One member of your team will put nitric acid (15.0 mL) in the Erlenmeyer flask while wearing plastic laboratory gloves. Then that person will drop a marble-sized ball of copper into the acid and immediately replace the stopper in the top of the flask. The other member of your team—also wearing plastic laboratory gloves—will collect orange NO_2 gas in the cuvette when it emits from the glass delivery tube at the other end of the apparatus. That person will quickly seal the tube with the screw cap. Both team members should efficiently exit the hood area to allow the next team to collect at the apparatus. Now you have your sample of NO_2 gas for this experiment.
2. Locate an available Spectronic 20 instrument. Take a cuvette containing only air and the cuvette containing your NO_2 gas sample to the instrument. Adjust the wavelength control of the instrument to 450 nm. Use the cuvette containing only air to zero the instrument (set zero absorbance). Measure and record the room-temperature absorbance of the NO_2 gas sample at 450 nm. Record the room temperature.

PHASE 2: Observation Over Time of Return to Room Temperature

3. Set up a warm-water bath with a 250-mL beaker on wire gauze on a tripod over a Bunsen burner. Fill the beaker with about 200 mL of water. Heat your water bath until the water is $\sim 20.0^{\circ}\text{C}$ above room temperature. Try to keep your burner flame smaller for a much gentler heating than you would use to boil water.
4. Partially immerse your NO_2 -filled cuvette in the water bath, using a test tube clamp and being careful to keep the screw cap entirely above the water. If any water gets into the cuvette it will convert your NO_2 gas back into nitric acid, and then you will have to get a new NO_2 sample. Modulate the heat supply to keep the bath temperature as close to $\sim 20.0^{\circ}\text{C}$ above room temperature as possible.
5. Once the NO_2 cuvette has been in the warm water bath ($\sim 20.0^{\circ}\text{C}$ above room temperature) for at least three minutes, one member of your team should locate an available Spectronic 20 instrument. That person should take the cuvette containing only air to the Spectronic 20 and zero the instrument as preparation for a series of measurements at a wavelength of 450 nm. If necessary, adjust the wavelength control to 450 nm before blanking the instrument. The other team member should measure the temperature of the warm water bath, and then remove the NO_2 -filled cuvette from the warm water bath. That person should quickly dry the cuvette with a paper towel and take the cuvette to the Spectronic 20 for measurement.
6. You will record the absorbance of the NO_2 cuvette over time: Record absorbance as soon as the cuvette is in the sample compartment of the Spectronic 20, then continue to record absorbance every 5 s for one minute. After the first minute, continue recording absorbance every 10 s for the next three minutes. (The time domain for your data should cover 0-240 s. You may want to prepare a data table in your lab notebook in advance for easier recording.)
7. Before proceeding examine your data from the previous series of measurements. The absorbance figures should exhibit a consistent trend. If you detect any inconsistencies in your data, please consult with your instructor about whether or not you should repeat these measurements.
8. Prepare an ice bath by filling a beaker with ice and water. Try to get the temperature down close to 0°C . (If all the ice melts, add more ice.)
9. Partially immerse the NO_2 -filled cuvette in the ice-water bath, using a test tube clamp to keep the screw cap entirely above the water. If any water gets into the cuvette you will need to get a new sample of NO_2 gas and restart at step 1 above.
10. Once the NO_2 cuvette has been in the ice-water bath for at least three minutes, one member of your team should locate an available Spectronic 20 instrument. That person should take the cuvette containing only air to the Spectronic 20 and zero the instrument as preparation for another series of measurements at a wavelength of 450 nm. The other team member should measure the temperature of the ice-water bath, and then remove the NO_2 -filled cuvette from the ice-water bath, dry the cuvette with a paper towel, and quickly take the cuvette to the Spectronic 20 for measurement.
11. You will again record absorbance over time: Record absorbance as soon as the cuvette is in the sample compartment of the Spectronic 20, then continue to record absorbance every 5 s for one minute. After the first minute, continue recording absorbance every 10 s for the next three

minutes. (The time domain for your data should again cover 0-240 s. You may want to prepare a data table in your lab notebook in advance for easier recording.) During this data acquisition stand by with a paper towel and every 30 s (immediately after recording a data point) remove the cuvette from the sample compartment, wipe off any condensation, and replace the cuvette in the sample compartment as quickly as possible. Continue timing during the wipe-off. If you miss an absorbance reading due to the wipe-off, just skip that point and record absorbance at the next planned time interval.

12. Before concluding the experiment, examine your data from the previous series of measurements. Again, the absorbance figures should exhibit a consistent trend. And both of your absorbance data series should approach the same absorbance value. If you detect any inconsistencies in your data, please consult with your instructor about whether or not you should repeat these measurements.
13. Take your NO₂-filled cuvette to the hood, open the screw cap, allow the gas to escape in the hood, and then rinse the cuvette with water. Turn in both cuvettes at the designated collection container.
14. After completing the procedure but before leaving lab, write in your notebook a brief statement (two to three sentences) on the quality and reasonableness of the data you collected. Note what you might do differently if you performed the lab again.

PHASE 3: Calculating Equilibrium Constants

You will start these calculations in the lab. Please read over this section BEFORE LAB so that you are prepared to do some immediate data analysis.

15. First, you will calculate the molar density (in mol/L) of NO₂ in the room temperature cuvette you measured in Phase 1 of this experiment. The molar absorptivity (ϵ) of NO₂ at 450 nm is equal to 2.95×10^2 L/mol•cm. Our cuvettes have 1.00-cm path length. Use these figures and your measured absorbance at room temperature to calculate the molar density of NO₂ in that cuvette from the Beer-Lambert Law.
16. Second, you will calculate the molar density of N₂O₄ in the room temperature cuvette you measured in Phase 1 of this experiment. The equilibrium constant (K_c) of the NO₂ dimerization reaction (see chemical reactions background section, above) has these near-room-temperature values (three significant figures):

T, °C	K_c
18.0	290
19.0	268
20.0	248
21.0	230
22.0	213
23.0	198
24.0	183
25.0	170

Use the molar density of NO_2 in your room temperature cuvette and the best value of K_c (closest temperature to your room temperature measurement) to calculate the molar density of N_2O_4 in that same cuvette.

17. Now that you have completely described the NO_2 - N_2O_4 system at room temperature, you can treat the $\sim 0.0^\circ\text{C}$ and $\sim 20.0^\circ\text{C}$ above room temperature systems you measured as changes to the room temperature system (since you measured the exact same sample of gases, just at different temperatures). Set up an equilibrium table (initial line, change line, and equilibrium line), using the molar densities in your room temperature cuvette as the initial amounts.
18. Next, calculate the molar density of NO_2 in your $\sim 20.0^\circ\text{C}$ above room temperature cuvette in the same way that you did above (in step 15). Use this as the final amount of NO_2 in your equilibrium table.
19. Based on the initial and final NO_2 amounts in your equilibrium table, figure out the change amount for NO_2 and then the change amount for N_2O_4 .
20. Now you can calculate the final amount of N_2O_4 in your equilibrium table based on the initial amount and the change amount. This is the molar density of N_2O_4 in your $\sim 20.0^\circ\text{C}$ above room temperature cuvette.
21. Use the molar densities of NO_2 and N_2O_4 in your $\sim 20.0^\circ\text{C}$ above room temperature cuvette to calculate the equilibrium constant (K_c) at $\sim 20.0^\circ\text{C}$ above room temperature.
22. Make another equilibrium table and repeat these calculations to determine the equilibrium constant (K_c) at $\sim 0.0^\circ\text{C}$.
23. You should now have three K_c values for the NO_2 - N_2O_4 system: $\sim 0.0^\circ\text{C}$, room temperature, and $\sim 20.0^\circ\text{C}$ above room temperature. Examine these results. There should be a consistent trend. If not, please describe your calculations to your instructor and ask for their advice.
24. Conclude your data analysis by graphing your data from Phase 2 of this experiment, both data series on the same set of axes. You will describe what this graph represents for your lab report. Your description should be consistent with the trend in your calculated K_c values.