PART 3

MORE GASES

OVERVIEW TO PART 3. MORE GASES

PART 3. MORE GASES

Generally, the gases described in Part 3 and the experiments that go with them should be conducted by individuals familiar and experienced with gas production using the syringe method introduced in Part 1. Five of the six gases in Part 3 have properties that make their proper use and handling more important than was the case for carbon dioxide, hydrogen and oxygen. Nitrogen, produced in Chapter 17 is not toxic, but traces of nitrogen oxides are usually produced as a byproduct of the reaction. For that reason, the production of nitrogen is included in this section on "intermediate-level gases".

CHAPTER 12 NITROGEN OXIDES

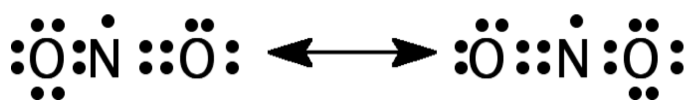
NITRIC OXIDE IS THE COMMON NAME for nitrogen monoxide, NO(g). Nitric oxide is a colorless, paramagnetic gas with an acrid odor and very low solubility in water. Its melting point is -163.6 ^oC and boiling point is -151.8 ^oC.

Nitric oxide is the simplest thermally stable odd-electron molecule known in chemistry. It is extremely reactive and readily oxidizes in air to produce nitrogen dioxide:

$$2NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

Both gases, nitric oxide and nitrogen dioxide, were discovered by Joseph Priestley in the 1770s.

Nitrogen dioxide is a red-brown paramagnetic gas that can be described with these two resonance forms:



The dynamic conversion between $NO_2(g)$ and $N_2O_4(g)$ makes it impossible to study either of these species alone:

$$2\ NO_2(g) \rightleftarrows N_2O_4(g) \qquad K_C^{25} = 215 \qquad \Delta H = -57\ kJ$$

In both forms, the nitrogen is in the +4 oxidation state. Dinitrogen tetroxide is a colorless, diamagnetic gas that dissociates reversibly as shown above. Its melting point is -11.2 ^oC and its boiling point is 21.2 ^oC.

Electrical discharges such as lightning produce NO(g) from nitrogen and oxygen. Automobiles also form NO(g). Nitric oxide rapidly oxidizes in air to form $NO_2(g)$ and these two gases are collectively called $NO_x(g)$. Tolerable levels of NO_x are less than 3 -

5 ppm. In Los Angeles where photochemical smog is particularly bad, levels have reached 0.9 ppm. A level of 500 ppm is fatal.

Nitric oxide is formed from the combustion of ammonia. Wilhelm Ostwald studied the production of nitric acid and by 1901 had perfected the following sequence of reactions:

$$4\ NH_3(g) + 5\ O_2(g) \rightarrow 4\ NO(g) + 6\ H_2O(g)$$

Nitrogen dioxide forms upon contact with air:

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

The primary use of these gases is to make nitric acid for the ultimate production of fertilizers and a wide range of useful chemicals. Nitric acid is formed by the reaction of $NO_2(g)$ with water, with which it reacts instantaneously. The NO(g) produced by this ***disproportionation*** reaction reacts with air to form more $NO_2(g)$, which in turn, reacts with water.

$$3NO_2 + H_2O(l) \rightarrow 2\ HNO_3(aq) + NO(g)$$

In terms of quantities, most of the nitric acid produced is reacted with ammonia to form ammonium nitrate for use as a fertilizer.

Nitric oxide, NO(g), is not very soluble in water. Only 0.00983 g NO(g) dissolve per L at 0 ^oC. This means that 14 mL of water will dissolve 1 mL NO(g). Nitrogen dioxide, however, actually reacts with water as discussed above.

Suitability

All of these experiments are suited for use as classroom demonstrations. Experiment 5 is ideally suited for use as a classroom demonstration using an overhead projector. Except for Experiment 8, which uses dangerous cryogenic materials, these experiments are also suited as laboratory experiments conducted by advanced high school or college-level students. These experiments are included in this chapter:

Experiment 1. Conversion of nitric oxide to nitrogen dioxide
Experiment 2. From nitrogen dioxide to nitric acid
Experiment 3. LeChatelier principle and the NO_2/N_2O_4 equilibrium
Experiment 4. High temperature favors the endothermic substance
Experiment 5. Acid rain microchemistry
Experiment 6. Acidic nature of nitrogen oxides
Experiment 7. Well plate reactions involving nitric oxide
Experiment 8. Dinitrogen trioxide is a blue liquid

Generally, the production of nitric oxide and nitrogen dioxide and the experiments that go with these gases should be conducted by individuals familiar and experienced with gas production using the syringe method introduced in Part 1. Both gases have properties that make their proper use and handling more important than was the case for carbon dioxide, hydrogen and oxygen.

All of these experiments serve to review basic concepts of chemistry including chemical properties, chemical changes, writing and working with chemical formulas, chemical reactions, and writing balanced chemical equations. In addition to these review topics, both nitric oxide and nitrogen dioxide are paramagnetic (odd-electron) molecules, an unusual property for most compounds. Nitrogen dioxide, like many paramagnetic substances, is colored and thus easy to see.

Experiment 1, "Conversion of nitric oxide to nitrogen dioxide", should be used to demonstrate the law of combining volumes (volume-volume relationships). The reaction is also mildly exothermic. Discussion should include mole calculations involving gases, bonding, molecular structure, polar molecules, and possibly environmental implications of nitrogen oxides, although this is covered in Experiment 5.

Experiment 2, "From nitrogen dioxide to nitric acid", addresses the chemical reaction that takes place between NO_2(g) and water. The reaction is an oxidation-reduction reaction. It is a good experiment to demonstrate the difference between solubility and chemical reaction because the reaction actually looks very much like the gas simply dissolving. Testing the solution shows that the reaction produces nitric acid.

Experiments 3 and 4 demonstrate aspects of LeChâtelier's principle. Both make better classroom demonstrations than laboratory experiments. Experiment 3 is subtle and benefits from the teacher's interpretation and Experiment 4 requires sources of hot and cold water and dovetails nicely with Experiment 3. The two can be done at the same time.

Experiment 5, "Acid Rain Microchemistry", is an excellent environmental chemistry experiment that can be used either as a classroom demonstration (with an overhead projector) or as a laboratory experiment.

Experiment 6 explores in more detail how nitric oxide is poorly soluble in water but very reactive with air to produce nitrogen dioxide, which is reactive with water. Chemical reactivity of gases, oxidation/reduction, and acid anhydrides are the focus of this experiment.

Experiment 7 is a follow-up to Experiment 6, but here instead of pure water, various solutions are used. Three of the four well-plate reactions described are oxidation-reduction reactions, and one involves complex ion formation.

In Experiment 8, "Dinitrogen trioxide is a blue liquid", a new unstable compound i9s produced by the reaction between nitric oxide and nitrogen dioxide. The experiment requires the use of liquid nitrogen or dry ice, and for that reason may be best performed as a classroom demonstration. The experiment demonstrates chemical formulas, chemical bonding, molecular structure, and chemical equilibrium.

Background skills required

Students should be able to:

- generate a gas as learned in Chapter 1.
- know how to prevent accidental/unintentional discharge of gas.
- understand fundamental concepts of high school chemistry so that observations can be interpreted.

Time required

These experiments require more than one laboratory period if students are conducting the experiments. Splitting the experiments between classroom demonstration and laboratory experiment is probably a good idea. For example, during one 45 minute laboratory period, students could do:

Preparation of Nitric Oxide
Experiment 1. Conversion of nitric oxide to nitrogen dioxide
Experiment 2. From nitrogen dioxide to nitric acid
Experiment 5. Acid rain microchemistry

The remaining experiments could be performed as classroom demonstrations or selected experiments could be performed during a second laboratory period.

Gas reaction catalyst tube

Three very interesting reactions involving nitrogen dioxide and the Gas Reaction Catalyst Tube were given in Chapter 18. Refer to these catalytic experiments:

F. Methane and nitrogen dioxide
G. Carbon monoxide and nitrogen dioxide

Website

This chapter is available on the web at website:

http://mattson.creighton.edu/Microscale_Gas_Chemistry.html

Instructions for your students

For classroom use by teachers. Copies of all or part of this document may be made for your students without further permission. Please attribute credit to Professors Bruce Mattson and Mike Anderson of Creighton University and this website.

PREPARATION OF NITRIC OXIDE[1]

General Safety Precautions

Always wear safety glasses. Gases in syringes may be under pressure and could spray liquid chemicals. Follow the instructions and only use the quantities suggested.

Toxicity

Nitric oxide immediately forms nitrogen dioxide upon contact with air. Thus, the toxicity of nitrogen dioxide is given here. Nitrogen dioxide has an irritating odor and is a poisonous gas. Concentrations of 100 ppm are dangerous. Concentrations greater than 200 ppm may be fatal. To put this in perspective, if the contents of one entire syringe of NO_2 (60 mL) were discharged into a volume of 1 m^3, the concentration of $NO_2(g)$ would be 60 ppm. Exercise caution when working with poisonous gases and vacate areas that are contaminated with unintentional discharges of gas.

Equipment

Microscale Gas Chemistry Kit (Chapter 1)

Chemicals

0.25 g $NaNO_2(s)$ per preparation

3 - 5 mL acidic ferrous sulfate solution (Instructions given below). To make ~40 mL of this solution for use by students, the following quantities of chemicals are needed:

- 13.5 g $FeSO_4 \cdot 7\ H_2O$
- 12 mL 6 M H_2SO_4
- 28 mL distilled water

1 M NaOH (4 g NaOH per 100 mL water)

O_2 is required to convert NO into NO_2

These quantities of reagents will produce approximately 60 mL of pure NO(g). The production of NO(g) is relatively fast and it typically takes about 30 seconds to fill a syringe with the gas. The reaction is:

$$2\ NaNO_2(s) + 2\ FeSO_4(aq) + 3\ H_2SO_4(aq) \rightarrow$$
$$2\ NO(g) + Fe_2(SO_4)_3(aq) + 2\ NaHSO_4(aq) + 2\ H_2O$$

[1] Content for this chapter first appeared as "Microscale Gas Chemistry, Part 5. Experiments with Nitrogen Oxides" Mattson, B. M.; Lannan, J. ***Chem13 News***, **255**, February, 1997.

The NO gas samples used in these experiments are generated by the In-Syringe Method described in Chapter 1 and summarized below. But first, we must make two solutions:

Preparation of Acidic Ferrous Sulfate Solution

To prepare enough acidic ferrous sulfate solution to perform the syringe reaction ten times, add 13.5 g $FeSO_4 \cdot 7\ H_2O$ to 28 mL distilled water. Add 12 mL 6 M H_2SO_4 and stir for a few minutes until all solid is dissolved. This produces a solution that is 1.8 M H_2SO_4 and 1.2 M Fe^{+2}(aq). (Alternatively, dissolve the ferrous sulfate in 36 mL water and then add 4 mL concentrated H_2SO_4. USE CAUTION! when handling concentrated H_2SO_4.)

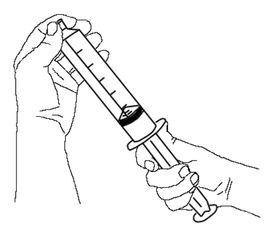
Preparation of Neutralization Solution

Prepare 100 mL of 1 M NaOH (4 g NaOH in H_2O to make 100 mL) in a 250 mL flask. Keep the flask stoppered when not in use. Label the flask "Neutralization Solution, 1 M NaOH". This solution will be used to neutralize excess reagents in the experiments.

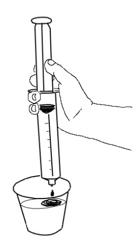
Preventing unwanted discharges of nitric oxide or nitrogen oxide

Both of these nitrogen oxides are noxious and must not be discharged into breathable air. The use of syringes to generate such gas samples works exceptionally well and far better than any other method in preventing undesired discharges. There are two simple considerations to keep in mind whenever handling noxious gases:

(1) When opening the syringe (by removing the syringe cap), do so with the plunger slightly withdrawn so the contents are under reduced pressure. Use your thumb to maintain the plunger in this position as shown in the drawing. This will allow some air to enter the syringe but no noxious gas to escape.



(2) After the gas sample has been generated, discharge the used reagents into a cup containing the ***Neutralization Solution***.



Step-by-step instructions for the preparation of nitric oxide

Each NO(g) preparation uses 0.25 g solid $NaNO_2$ and a minimum of 3 mL of the acidic ferrous sulfate solution. The volume of NO produced is approximately 60 mL. Before starting, have these items ready: your microscale gas kit, the two reagents needed, and the Neutralization Solution.

1. Wear your safety glasses!
2. Make sure the plunger moves easily in the barrel. If it binds or sticks, try a different combination of plunger and barrel.
3. Measure out 0.25 g solid $NaNO_2$. Place the solid directly into the vial cap to prevent loss.
4. Fill the syringe barrel with water. Place your finger over the hole to form a seal.
5. Float the vial cap containing the solid reagent on the water surface.
6. Lower the cap by flotation. Release the seal made by finger to lower the cap into the syringe barrel without spilling its contents.
7. Install the plunger while maintaining the syringe in a vertical position, supported by the wide-mouth beverage bottle or flask.
8. Fill the weighing dish with the Acidic Ferrous Sulfate Solution. Draw 5 mL of this solution into the syringe.
9. Push the syringe fitting into the syringe cap.
10. Shake the device up and down in order to mix the reagents. Gently help the plunger move up the barrel. Upon mixing the reagents in the syringe with vigorous shaking, gaseous NO is quickly produced. A trace of reddish NO_2 is observed at first but soon disappears. The aqueous solution turns black in color.
11. With the plunger slightly withdrawn to assure reduced pressure inside the syringe, and with the syringe held “cap-up”, remove the syringe cap.
12. Discharge the liquid reagent into the Neutralization Solution. Immediately cap the syringe to prevent loss of gas.
13. Wash away contaminants. Nitric oxide-filled syringes must be “washed” in order to remove traces of unwanted chemicals from the inside surfaces of the syringe before the gases can be used in experiments. Remove the syringe cap and draw 5 mL water into the syringe. Cap the syringe and shake to wash inside surfaces. Remove cap and discharge water only (no gas), and recap the syringe. Repeat these washing steps if necessary.

Disposal of NO(g) and NO_2(g) Samples

Unwanted NO(g) and NO_2(g) samples can be destroyed by drawing some water into the syringe, followed by discharging the syringe solution into the Neutralization Solution.

Teaching tips

1. Instructor should prepare the Acidic Ferrous Sulfate Solution for the entire class.
2. Review with the class the ***safe*** method for removing the cap in the event more than 60 mL of gas is going to be produced. The cap must be directed upward before removal. The reagents should be discharged into the Neutralization Solution.

Questions

1. Calculate the amount of sodium nitrite used (in moles).
2. Given that sodium nitrite is the limiting reagent, what quantity, in moles, of nitric oxide is expected?
3. Use the ideal gas law to convert your answer from Question 2 into a volume, expressed in mL. Unless better values are available, you may assume that the reaction took place at standard pressure and 25 ^{o}C.
4. How does the calculated volume of nitric oxide compare with the experimentally obtained volume? Determine the percent yield.

Advanced Questions

5. Assign oxidation numbers to the reaction that occurred in order to produce nitric oxide. What was the oxidizing agent? The reducing agent?

EXPERIMENTS WITH NITROGEN OXIDES

Experiments 2, 5 and 6 use universal indicator solution or red cabbage solution to estimate pH. Prepare a solution by mixing 200 mL distilled water plus 20 mL universal indicator solution. Raise the pH to 8 by bubbling through the solution a pipetful of gaseous ammonia taken from the vapors above a solution of concentrated ammonium hydroxide solution. The following chart provides indicator colors vs. the corresponding pH.

Indicator Colors		
pH	**Universal**	**Red Cabbage**
4.0	Red	Red
5.0	Orange Red	Purple
6.0	Yellow Orange	Purple
7.0	Dark Green	Purple
8.0	Light Green	Blue
9.0	Blue	Blue-Green
10.0	Reddish Violet	Green
11.0	Violet	Green
12.0	Violet	Green
13.0	Violet	Green-Yellow
14.0	Violet	Yellow

EXPERIMENT 1. CONVERSION OF NITRIC OXIDE TO NITROGEN DIOXIDE

Equipment

Microscale Gas Chemistry Kit

Chemicals

NO(g), 40 mL

O_2(g), 20 mL (Chapter 4 or 5)

Suitability

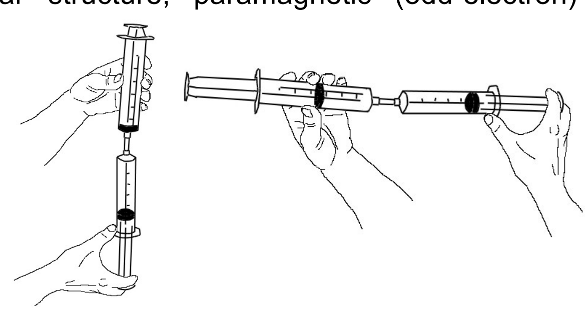
high school lab, university lab, and classroom demonstration

Applications, Topics, Purpose

law of combining volumes (volume-volume relationships), chemical properties of nitric oxide, energy changes, chemical formulas, mole calculations involving gases, chemical reactions, bonding, molecular structure, paramagnetic (odd-electron) molecules

Instructions

Transfer the NO(g) to a clean, dry syringe via a short length of tubing as shown in the figure. Simultaneously push and pull on the respective plungers. (This step is



necessary because water readily dissolves NO_2.)

Connect the NO(g)-filled syringe with the O_2(g)-filled syringe via a short length of clean, dry tubing. Slowly transfer a volume of O_2(g) equal to half of the volume on the NO(g). The reaction is:

$$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g) \qquad \Delta H = -56.4\ kJ$$

IMPORTANT! The NO_2(g) gas produced in this way will be used in the next several experiments.

Teaching tips

1. Note that the NO/NO_2 syringe becomes warmer as a result of the reaction.
2. Note that the volume of NO_2(g) is equal to the initial volume of NO(g). Discuss the law of combining volumes.

Questions

1. Write the balanced chemical equation for the reaction that occurred in the syringe when NO(g) to O_2(g) were combined.
2. Was the reaction endothermic or exothermic? Was the reaction kinetically fast or slow?
3. If one were to add 20 mL of O_2(g) to 40 mL of NO(g), would the final volume be 60 mL total?
4. What final ***total*** volume of gas is expected if 10 mL of NO(g) and 30 mL of O_2(g) were allowed to react?
5. The law of combining volumes is based on the fact that volume, V, is directly proportional to the number of moles, n, of gas at constant temperature and pressure. How might this be useful in chemical industry?

EXPERIMENT 2. FROM NITROGEN DIOXIDE TO NITRIC ACID

Equipment

Microscale Gas Chemistry Kit

Chemicals

$NO_2(g)$, >20 mL

universal indicator

Suitability

high school lab, university lab, and classroom demonstration

Applications, Topics, Purpose

chemical formulas, chemical reactions, writing balanced chemical equations, classifying chemical changes, properties of NO(g) and $NO_2(g)$, chemical reactivity of NO(g) and $NO_2(g)$, polar molecules, paramagnetic (odd-electron) molecules, acid anhydrides, acid preparation, oxidation-reduction reactions

Instructions

The reaction between nitrogen dioxide and water to produce nitric acid involves a oxidation-reduction reaction and is more complicated than expected:

$$3\ NO_2(g) + H_2O(l) \rightarrow 2\ HNO_3(aq) + NO(g)$$

The NO(g) produced is not very water-soluble, but quickly reacts with oxygen from air as per Experiment 1:

$$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

This in turn reacts with more water. With each cycle, $^2/_3$ of the nitrogen dioxide is converted to nitric acid.

Draw 20 mL water into a syringe containing NO_2. Even though the gas appears to be dissolving in the water, it is actually reacting with water to produce nitric acid. Additional water is drawn into the syringe as the red colored gas disappears. Test the acidity of the resulting solution with universal indicator.

Teaching tips

1. Work with the students to help them understand the "cycle" of reactions presented in the Instructions.
2. The color chart for universal indicator and red cabbage indicator is provided at the beginning of this section.

Questions

1. Did the universal indicator solution show the solution to be acidic?
2. How does dissolving differ from reacting?
3. Did all of the gas in the syringe react? Why not?
4. Combine the two reactions given in the Instructions to give the overall reaction.

Experiment 3. LeChâtelier principle and the NO_2/N_2O_4 equilibrium

Equipment

Microscale Gas Chemistry Kit

Chemicals

NO_2(g), 30 mL

Suitability

high school lab, university lab, and classroom demonstration

Applications, Topics, Purpose

LeChâtelier's principle, chemical properties of gases, enthalpy vs. entropy, kinetics, dissociation, chemical reactions, chemical bonding, molecular structure, rates of chemical reactions (chemical kinetics), activation energy, chemical equilibrium

Instructions

Nitrogen dioxide is a brownish-red gas that exists in equilibrium with its dimer, N_2O_4(g):

$$2\ NO_2(g) \rightleftarrows N_2O_4(g) \qquad K_c^{25} = 215 \qquad \Delta H = -57\ kJ$$

Quickly pull the syringe barrel outward to the 60 mL mark and hold it in that position. The NO_2(g) will immediately, but only momentarily fade due to the decrease in concentration but within a fraction of a second the red color will intensify due to formation of more NO_2 as predicted by the LeChâtelier principle.

Predict what will happen if you push the plunger down rapidly and firmly and hold it in that position. Now try it!

Teaching tips

1. LeChâtelier's principle states that an increase in volume will favor a shift in the direction of the greater number of moles of gas. If this is so, the gas sample should become more reddish, which is counter-intuitive because increasing the volume usually means that the concentration has been "diluted".

2. There will always be a mixture of the two gases with N_2O_4(g) being the dominant species at 25 °C (Note K_c^{25} = 215). The color (red-brown) of the gas mixture will change in its intensity when the equilibrium is shifted right (lighter) or left (darker). Careful observation is needed to observe the change of color intensity of the gases in the syringe.

3. N_2O_4(g) consists of two NO_2 molecules joined by a N-N bond. The bond strength is 57 kJ/mol. In terms of enthalpy, the equilibrium would prefer to be in the dimer form. In terms of entropy, the two monomers are preferred.

Questions

1. What color change did you observe in the first instant when the volume was decreased? What happened next? Explain these observations.

2. $N_2O_4(g)$ consists of two NO_2 molecules joined by a N-N bond. Is the dissociation of $N_2O_4(g)$ into the two NO_2 molecules exothermic or endothermic? Is it true that the breaking of *any* bond is an endothermic process?

Advanced Questions

3. Look up the nitrogen-nitrogen single bond energy in your chemistry book. How does it compare with the value given in the Instructions above, $\Delta H = -57$ kJ?

4. Sketch the Lewis dot structure for both NO_2 and N_2O_4. Include resonance when appropriate. What is the nitrogen-oxygen bond order?

5. If 0.10 mol N_2O_4 were placed in a 1.0 L flask and allowed to come to equilibrium, calculate the concentrations of both NO_2 and N_2O_4 at 25 ^oC, given the equilibrium expression and value for K_c^{25}.

EXPERIMENT 4. HIGH TEMPERATURE FAVORS THE ENDOTHERMIC SUBSTANCE

Equipment

Microscale Gas Chemistry Kit
cup of very hot water and cup of ice cold water

Chemicals

two syringes $NO_2(g)$, 30 mL each

Suitability

high school lab, university lab, and classroom demonstration

Applications, Topics, Purpose

LeChâtelier's principle, chemical properties of gases, enthalpy vs entropy, kinetics, dissociation, chemical reactions, chemical bonding, molecular structure, rates of chemical reactions (chemical kinetics), activation energy, chemical equilibrium

Instructions

Place a syringe of NO_2/N_2O_4 mixture in hot water and another one in cold water. Determine whether hot water favors $NO_2(g)$ or $N_2O_4(g)$. Does cold water favor the opposite?

$$2\,NO_2(g) \rightleftarrows N_2O_4(g) \qquad K_c^{25} = 215 \qquad \Delta H = -57\text{ kJ}$$

Teaching tips

See Teaching Tips from previous experiment.

Questions

1. Why did the red-brown color intensify when the gas was heated? Explain this by using the enthalpy change for the reaction:

$$2\ NO_2(g) \rightleftharpoons N_2O_4(g) \qquad K_c^{25} = 215 \qquad \Delta H = -57\ kJ$$

2. Is the reaction written above exothermic or endothermic?

3. Would an increase in temperature produce more $NO_2(g)$ or $N_2O_4(g)$?

Advanced Questions

4. Determine K_c^{25} and ΔH for the reaction:

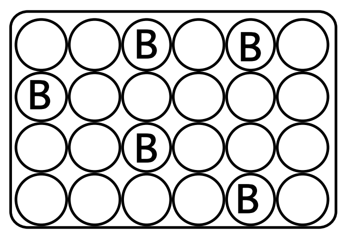
$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g) \qquad K_c^{25} = ? \qquad \Delta H = ?$$

5. The color change occurs quickly — somewhat limited by the time it takes the syringe to warm/cool. Sketch a reaction profile diagram that shows the relative energies of $N_2O_4(g)$ and $NO_2(g)$. Should the activation energy be large or small?

EXPERIMENT 5. ACID RAIN MICROCHEMISTRY

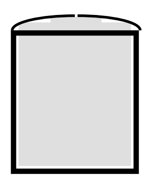
Equipment

Microscale Gas Chemistry Kit 24-well plate
1-gallon (4 L) sealable plastic food storage bag
overhead projector (if used as a classroom demo)



Chemicals

$NO_2(g)$, 30 mL
universal indicator, 5 mL
sodium bicarbonate, $NaHCO_3$, 0.1 g



For use on an overhead projector: overfill the wells

Suitability

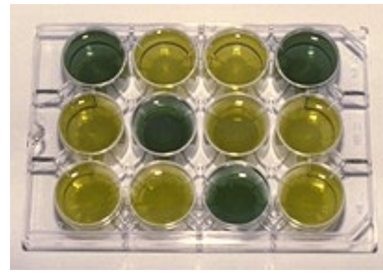
high school lab, university lab, and demo

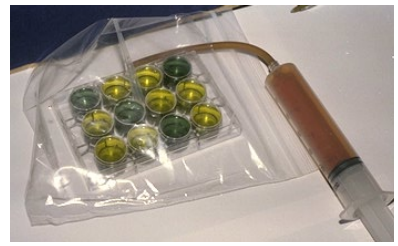
Applications, Topics, Purpose

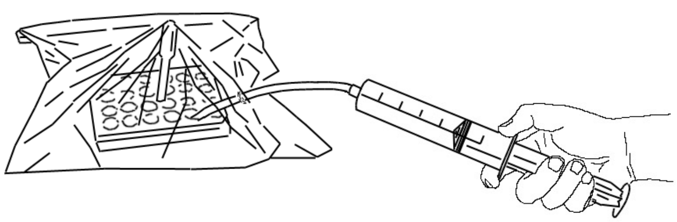
environmental chemistry, acid-base reactions, effusion/diffusion, acid anhydrides

Instructions

Automobiles produce nitrogen oxides that act to produce acid rain. In this experiment, a 24-well plate is enclosed in a sealable bag to create an ecosystem. Mix 100 mL distilled water with 5 mL of universal indicator solution. Fill ~15 - 18 of the wells with this solution. Use a plastic pipet to add the final drops to each well. To the remaining universal indicator solution, dissolve 0.1 g of sodium bicarbonate, $NaHCO_3$. Fill the remaining six wells with this solution. Place a 10 cm length of a plastic pipet between the four middle wells in order to prop up the bag above the surface of the filled wells. Slip the filled well plate and the syringe into the plastic bag. Seal the bag shut. Place the assembly on the overhead projector. Use a pencil or similar sharp object to poke a small hole through a 4 L (1 gallon) sealable plastic bag. Work the tubing through the hole. Discharge the gas into the bag. As the gas drifts across the "landscape", the unbuffered lakes will become acidic. The buffered lakes will eventually become acidified as well. At the end of the experiment, shake the contents of the bag to dissolve all of the NO_2. Open the bag and discard the contents down the drain.







Teaching tips

1. Notice the difference between the buffered and the unbuffered lakes.
2. The bicarbonate ion, $HCO_3^-(aq)$ of sodium bicarbonate is a base in water.
3. Most lakes are naturally slightly alkaline due to sedimentary materials, which contain carbonates. Acid rain causes the pH of lakes to drop to levels in which microorganisms cannot survive. Because many of the microorganisms affected form the foundation of the food chain, all life in the lake suffers.

Questions

1. What was the pH of the buffered and unbuffered lakes before adding the $NO_2(g)$? How does the pH change for each kind of lake during the first ten minutes after addition of the $NO_2(g)$?

2. What is the function of a buffer?

3. Which natural lake would be more affected by acid rain: a rock-bottomed lake with little mineral content in the water or a limestone-bottomed lake which serves as a source of a certain amount of carbonate ion?

EXPERIMENT 6. ACIDIC NATURE OF NITROGEN OXIDES

Equipment

Microscale Gas Chemistry Kit
1-gallon (4 L) sealable plastic food storage bag

Chemicals

$NO_2(g)$, 60 mL
2 mL universal indicator
ammonium hydroxide (only the fumes above the liquid will be used)

Suitability

advanced high school lab, university lab, and classroom demonstration.

Applications, Topics, Purpose

environmental chemistry, effusion/diffusion, acid anhydrides, chemical reactivity of $NO_2(g)$ and $NO(g)$, polar molecules

Instructions

Nitrogen dioxide, $NO_2(g)$ is the acid anhydride of nitric acid. The following disproportionation reaction with water is instantaneous and is the final step in the Ostwald Process.

$$3\ NO_2(g) + H_2O(l) \rightarrow 2\ HNO_3(aq) + NO(g)$$

Poke a small hole with a pencil through the plastic food storage bag. Moisten one end of the 15 cm piece of tubing and work it through the hole. About half of the tubing should be inside the bag.

Prepare a solution of 100 mL distilled water and 2 mL universal indicator in a 250 mL beaker. Add a trace of $NH_3(g)$ (one or more pipetfuls of NH_3 ***vapors*** taken from the headspace above an ammonium hydroxide solution is bubbled through the indicator solution. Repeat if necessary until a purple color results.) Place cup of solution in a plastic bag and seal shut. Connect the tubing to the syringe and slowly dispense the

NO(g) below the surface of the dilute NH_3(aq). The NO(g) will react with O_2(g) from the air and then settle on the surface of the water where it reacts, making nitric acid and NO(g) according to the above equation. The NO(g) reacts with O_2(g) from the air and the cycle continues. The solution becomes acidic near the surface creating layers of colors.

At the end of these experiments, allow the bag to stand overnight. The NO_2 produced from the reaction of NO with air will all react with the large amount of water. Open the bag and discard the contents down the drain.

Teaching tips

1. Describe the Ostwald process and the importance of nitric acid in society — its use in fertilizers, explosives, chemical manufacture, etc.
2. The experiment works because (a) NO(g) does not dissolve in water, hence the bubbles make it to the surface; (b) NO_2(g) reacts instantaneously with the oxygen in air to produce NO_2(g); (c) the resulting NO_2(g) is much heavier than air so stays relatively close to the surface of the water; and (d) reacts instantly with water at the water-air interface. Layers are sometimes noticed because the reaction took place just at the air-water interface.
3. The overall reaction (Advanced Question #3, below) is:

$$4\ NO(g) + 2\ H_2O(l) + 3\ O_2(g) \rightarrow 4\ HNO_3(aq)$$

Questions

1. Draw a sketch of the reaction apparatus. Show the bubbles and label the chemical composition of the bubbles.
2. Refer again to the figure you drew for the previous question. The experiment works because of the following factors. Show each of these factors on your diagram.
   - NO(g) does not dissolve in water, hence the bubbles make it to the surface;
   - NO_2(g) reacts instantaneously with the oxygen in air to produce NO_2(g);
   - The resulting NO_2(g) is much heavier than air so stays relatively close to the surface of the water; and
   - NO_2(g) reacts instantly with water at the water-air interface.

Advanced Questions

3. Given the following two equations that are taking place:

$$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

$$3\ NO_2(g) + H_2O(l) \rightarrow 2\ HNO_3(aq) + NO(g)$$

Determine the coefficients for the overall reaction:

$$\_\_\_ NO(g) + \_\_\_ H_2O(l) + \_\_\_ O_2(g) \rightarrow \_\_\_ HNO_3(aq)$$

4. Explain why the reaction between two gaseous molecules such as NO(g) and O_2(g) is always faster than the reaction between a gas such as NO_2(g) and a liquid such as H_2O(g) Assume that both reactions have small activation energies — i.e., large rate constants. By extension, would you expect the reaction between a gas and a solid to be faster or slower than the reaction between two gases? Which is faster, all other factors being equal, the reaction between two liquids or the reaction between a liquid and a solid? Reactions that would otherwise be fast, but are slowed because one of the reagents has poor mobility, are called *diffusion-limited* reactions.

EXPERIMENT 7. WELL PLATE REACTIONS INVOLVING NITRIC OXIDE

Equipment

Microscale Gas Chemistry Kit
12 or 24-well plate
1-gallon (4 L) sealable plastic bag

Chemicals

NO(g), 60 mL
Neutralization Solution
2 mL faintly pink $KMnO_4$(aq) (one small crystal of $KMnO_4$ in 50 mL water)
2 mL Br_2(aq); (See Appendix D)
2 mL dilute Fe^{+2}(aq): (2 mL water + 2 - 3 small crystals $FeSO_4 \cdot 7H_2O$)
2 mL I^-(aq); (2 mL water + approximately 0.1 g KI)

Suitability

advanced high school lab, university lab, and classroom demonstration.

Applications, Topics, Purpose

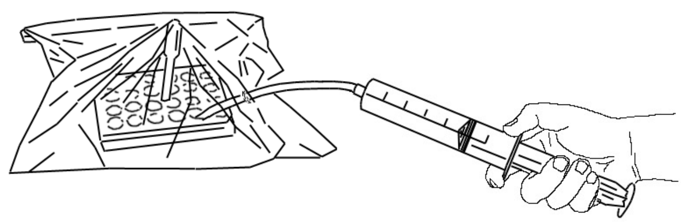
environmental, oxidation-reduction reactions, complex ion formation, chemical formulas, chemical reactions, writing balanced chemical equations, classifying chemical changes, properties and chemical reactivity of NO(g) and NO_2(g)

Instructions

The following reactions are performed in a 12 or 24-well plate. Prepare the following reagents in separate wells before generating NO(g).

Test tube:	*Contains:*
1	2 mL faintly pink $KMnO_4$(aq)
2	2 mL Br_2(aq)
3	2 mL Fe^{+2}(aq)
4	2 mL I^-(aq)
5	Rinse water; > $^3/_4$ full
6 - 8	Neutralization Solution (1 M NaOH) Fill these three wells > $^3/_4$ full

One syringe full of NO(g) should be adequate to complete all four of these experiments. Generate NO(g) as described above. Wash the gas thoroughly. Replace the syringe cap with a 15 cm length of tubing. Use a pencil or similar sharp object to poke a small hole through a 4 L (1 gallon) sealable plastic bag. Work the tubing through the hole. Place the filled well plate inside the bag and zip shut. Into each well slowly discharge enough NO(g) through the solution to achieve the desired results. Rinse the tubing before going on to the next well.



At the end of these experiments, allow the bag to stand overnight. The NO_2(g) produced from the reaction of NO(g) with air will react with the Neutralization Solution in Wells 6 - 8. Open the bag and discard the contents to the Neutralization Solution.

Although NO(g) is not very soluble in water, in the first two experiments, NO(g) is being oxidized by the powerful oxidizing agents permanganate and bromine, respectively.

NO(g) reacts with $KMnO_4$(aq)

In this case, nitric oxide is oxidized by $KMnO_4$(aq) to produce either colorless Mn^{+2}(aq) or a brown MnO_2 precipitate, depending on the conditions. The NO(g) is oxidized to nitrate ion:

$$5\ NO(g) + 3\ MnO_4^-(aq) + 4\ H^+(aq) \rightarrow 5\ NO_3^-(aq) + 3\ Mn^{+2}(aq) + 2\ H_2O \quad E^o = +\ 0.55\ v$$

or

$$NO(g) + MnO_4^-(aq) \rightarrow NO_3^-(aq) + MnO_2(s) \quad E^o = +\ 0.72\ v$$

NO(g) reduces Br_2(aq) to colorless bromide

The reaction is:

$2\ NO(g) + 3\ Br_2(aq) + 4\ H_2O \rightarrow 2\ NO_3^-(aq) + 6\ Br^-(aq) + 8\ H^+(aq)$ $E^o = +\ 0.11\ v$

NO(g) reacts with Fe^{+2}(aq)

Nitric oxide(g) reacts with Fe^{+2}(aq) to produce the "brown ring test" compound, $[Fe(H_2O)_5(NO)]^{+2}$(aq):

$$NO(g) + [Fe(H_2O)_6]^{+2}(aq) \rightarrow [Fe(H_2O)_5(NO)]^{+2}(aq) + H_2O(l)$$

The $[Fe(H_2O)_5(NO)]^{+2}$(aq) appears as a brown solution that darkens to a green hue and eventually precipitates, presumably as a ferric compound.

NO(g) oxidizes I^-(aq)

As we noted in the previous experiment, when NO(g) bubbles through the aqueous solution, some reaction takes place between the gas bubble-solution interface, however, most of the NO(g) leaves the solution unreacted. Then, upon exposure to air, NO is quickly converted to NO_2(g):

$$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

The NO_2(g) soon reacts with water:

$$3\ NO_2(g) + H_2O(l) \rightarrow 2\ HNO_3(aq) + NO(g)$$

The NO(g) thus produced reacts with more O_2(g), and the cycle is repeated. The overall reaction is:

$$4\ NO(g) + 2\ H_2O(l) + 3\ O_2(g) \rightarrow 4\ HNO_3(aq)$$

Aqueous nitric acid, HNO_3(aq), is a strong oxidizing agent. When looking at a table of reduction potentials, the nitrate ion has a large, positive reduction potential:

$$NO_3^-(aq) + 4\ H^+(aq) + 3\ e^- \rightarrow NO(g) + 2\ H_2O(l) \quad E^o = +0.96\ V$$

Given that nitric oxide, air and water produce nitric acid as per the above discussion, the reaction with I^- (aq) is:

Reduction half: $NO_3^-(aq) + 4\ H^+(aq) + 3\ e^- \rightarrow NO(g) + 2\ H_2O(l) \quad E^o = +0.96\ V$

Oxidation half: $2\ I^-(aq) \rightarrow I_2(s) + 2\ e^- E^o = -0.54\ V$

Overall reaction:

$2\ NO_3^-(aq) + 8\ H^+(aq) + 6\ I^-(aq) \rightarrow 2\ NO(g) + 4\ H_2O(l) + 3\ I_2(s) \quad E^o = +0.42\ V$

Teaching tips

1. The expected results/observations are:
   - The well plate containing $KMnO_4$(aq) should turn colorless (or brown ppt).
   - The well plate containing bromine water should turn clear.
   - The well plate containing $FeSO_4$(aq) should turn dark brown.
   - The well plate containing KI(aq) should turn yellow.
2. Students ask about the potassium ion in KI(aq) or $KMnO_4$(aq) or the sulfate ion in the well containing the iron (II) sulfate. In the reactions involving these compounds, the potassium and sulfate ions act as spectator ions. Provide net-ionic equations to the students.

Questions

1. Did you see a chemical change in the four wells after NO(g) was added? Describe each.
2. In the reaction with KI, what compound causes the solution to be yellow?
3. What is the oxidation number of the nitrogen atom in both NO(g) and NO_3^-(aq)?
4. Does the NO(g) act as an oxidizing or reducing agent when it reacts with the Br_2(aq)?
5. The brown compound obtained in the reaction between NO and $FeSO_4$(aq) is called the ***brown ring*** test. How might this test be useful as a chemical method of qualitative analysis?

EXPERIMENT 8. DINITROGEN TRIOXIDE IS A BLUE LIQUID

Equipment

Microscale Gas Chemistry Kit

Chemicals

NO(g), 60 mL
O_2(g), 30 mL (Chapter 4 or 5)
liquid nitrogen or a dry ice/alcohol bath
Neutralization Solution

Suitability

advanced high school lab, university lab, and classroom demonstration.

Applications, Topics, Purpose

physical and chemical changes and properties, chemical formulas, chemical reactions, chemical bonding, molecular structure, chemical equilibrium

Instructions

Either liquid nitrogen or a dry ice/alcohol bath is needed as a source of extreme cold for this experiment.[1] (A ice/salt bath at a temperature below -10 ^oC will also work, although not as well.)

Dinitrogen trioxide is a blue liquid produced by the combination of equal quantities of NO(g) and NO_2(g):

$$NO(g) + NO_2(g) \rightleftarrows N_2O_3(l) \qquad mp = -102\ ^oC$$

Dinitrogen trioxide partially disproportionates into NO(g) and NO_2(g) at temperatures above 4 ^oC according to the following equilibrium. The disproportionation is reversible and becomes extensive as the temperature increases.

$$N_2O_3(l) \rightleftarrows NO(g) + NO_2(g)$$

The preparation of N_2O_3(l) is conveniently accomplished in one step by combining 4 volumes of NO(g) with 1 volume of O_2(g) with suitable cooling:

$$4\ NO(g) + O_2(g) \rightleftarrows 2\ N_2O_3(l)$$

To do this, prepare a syringe of O_2(g) and set it aside. In another syringe, prepare 60 mL NO(g) from 0.25 g solid $NaNO_2$ and 3 - 4 mL of the acidic ferrous sulfate solution. Wash the NO(g) several times and transfer it to a clean, dry syringe. Connect the NO(g) and O_2(g) filled syringes with a short length of tubing. Slowly transfer a volume of O_2(g) equal to one fourth the volume on the NO(g). Thus, 60 mL NO(g) would require 15 mL O_2(g).

The volume of the N_2O_3(g) expected from the above chemical equation is half that of the initial volume of NO(g): 4 moles of NO produces 2 moles of N_2O_3. Even though the N_2O_3(g) is actually in an equilibrium mixture with NO(g) + NO_2(g), the volume of the products is less than that of the initial NO(g). As the reaction takes place, you should note that the tubing collapses, indicating that the pressure within the assembly of the two joined syringes is less than the external pressure. Usually the plungers will move inward as well.

Place the capped syringe of N_2O_3 (= NO_2 + NO) into the cold bath or liquid nitrogen to a depth of about 2 - 3 cm (to the 15 mL mark on the syringe.) Allow the syringe to remain in the cold until you notice that the plunger is beginning to move inward. Droplets of blue liquid or solid N_2O_3 will appear. Allow the syringe to warm to room temperature. Reddish NO_2(g) will reappear.

The NO_x(g) produced can be destroyed by slowly bubbling it through the Neutralization Solution.

[1] Prepare a dry ice/propanol bath in a 400 mL beaker: Add 250 mL 2-propanol (ordinary rubbing alcohol) to the beaker and slowly add small chunks of dry ice until the dry ice persists in the solution.

Teaching tips

1. This makes a good classroom demonstration. Both liquid nitrogen and dry ice are dangerous substances that should only be handled by responsible students or instructors.

Questions

1. Sketch the Lewis dot structure of NO_2, NO, and N_2O_3.

2. What distinguishes N_2O_3 from NO_2 and NO?

3. In experiment 3 you looked up the nitrogen-nitrogen bond energy. What was that value? If the nitrogen-nitrogen bond is broken, is energy released or absorbed? If the latter, where does this energy come from?

Clean-up and storage.

At the end of the experiments, clean the syringe parts, caps and tubing with water. Rinse all parts with distilled water if available. Be careful with the small parts because they can easily be lost down the drain. **Important:** Store plunger out of barrel unless both are completely dry.

SUMMARY OF MATERIALS AND CHEMICALS NEEDED FOR CHAPTER 12. EXPERIMENTS WITH NITROGEN OXIDES.

Equipment and materials required

Item	For Demo	For 5 pairs	For 10 prs
Microscale Gas Chemistry Kit	1	5	10
24-well plate	1	5	10
1-gallon (4 L) sealable plastic food storage bag	1	5	10
overhead projector*	*	-	-

* if Experiment 5 is used as a classroom demonstration

Chemicals required

Item	For Demo	For 5 pairs	For 10 prs
sodium nitrite, $NaNO_2$	2 g	10 g	20 g
ferrous sulfate heptahydrate, $FeSO_4 \cdot 7\ H_2O$	15 g	15 g	30 g
dilute sulfuric acid, dilute, 6 M H_2SO_4	15 mL	15 mL	30 mL
sodium hydroxide, M NaOH	5 g	25 g	50 g
potassium iodide, KI, powder	1 g	5 g	10 g
6% hydrogen peroxide H_2O_2(aq)*	20 mL	100 mL	200 mL
ice water	1 cup	5 cups	10 cups
universal indicator	5 mL	25 mL	50 mL
ammonium hydroxide	a	a	a
sodium bicarbonate, $NaHCO_3$	0.1 g	1 g	2 g
potassium permanganate, $KMnO_4$	0.1 g	0.1 g	0.1 g
potassium iodide, KI	0.1 g	0.1 g	0.1 g
liquid nitrogen or a dry ice + alcohol bath	b	b	b
bromine water	c	c	c

a. only the NH_3 fumes from the concentrated ammonium hydroxide solution will be used
b. 100 mL or 200 g/100 mL
c. see Appendix D. Use 0.1 g sodium bromide, NaBr, 1 mL 1 M HCl and 1 mL sodium hypochlorite (household laundry bleach)