Temperature Equilibrium Tubes

LeChâtelier's Principle

Introduction

Many important reactions that take place in the atmosphere involve equilibrium concentrations of gas-phase reactants and products. How does temperature affect the position of equilibrium for the dimerization reaction of nitrogen dioxide?

Concepts

- Chemical equilibrium
- Gas-phase reactions
- LeChâtelier's principle
- Nitrogen oxides

Materials

Acetone	Beakers, borosilicate glass, 1-L, 6
Dry Ice	Dewar flask
Equilibrium tubes, Nitrogen dioxide, 4*	Hot plate
Ice	Support stands, 4
Kosher (rock) salt	Thermal gloves (Zetex™)
Liquid nitrogen	Utility clamps, 4

**The commercially produced nitrogen dioxide tubes are made of Pyrex® glass and are temperature- and shock-resistant.*

Safety Precautions

Nitrogen dioxide is a highly toxic gas. Sealed Pyrex® demonstration tubes containing nitrogen dioxide are available commercially. The Pyrex tubes are temperature- and shock-resistant. Exercise great care when working with the nitrogen dioxide equilibrium tubes so they do not crack or break. Clamp the tubes in a fixed position in the higher temperature baths so the tubes will not "jump" out of the baths. Avoid subjecting the tubes to extreme changes in temperature (i.e., do not transfer a tube from a very cold bath to a boiling water bath). Dry ice–acetone and liquid nitrogen baths are extremely cold and will cause frostbite. Wear Zetex™ safety gloves that are specially designed for working with high and low temperatures. Wear chemical splash goggles, temperature-resistant gloves and chemical-resistant apron. Please consult current Safety Data Sheets for additional safety, handling and disposal information.

Preparation

1. Prepare four baths of different temperatures in 1-L borosilicate glass beakers. Convenient choices are described in the following steps.
2. Fill three beakers approximately half-full with water. Place a boiling stone in one beaker and heat it on a hot plate to prepare a boiling water bath. Add crushed ice to the second beaker to prepare an ice water bath (0 °C), and use rock salt and crushed ice in a third beaker to prepare a below-zero temperature bath (approximately –15 °C).
3. The observed temperature effect on the position of equilibrium for the dimerization reaction of nitrogen dioxide is greatly enhanced by using very low temperature baths (dry ice–acetone or liquid nitrogen). Fill a beaker approximately ⅓ full with acetone, and add small chunks of dry ice to obtain a –77 °C bath. Use liquid nitrogen in a Dewar flask to demonstrate the effect at –196 °C.

Procedure

Demonstrate the reversibility of the NO_2/N_2O_4 reaction by placing the demonstration tubes in baths of different temperatures and observing the color changes.

Disposal

Please consult your current *Flinn Scientific Catalog/Reference Manual* for general guidelines and specific procedures, and review all federal, state and local regulations that may apply, before proceeding. The nitrogen dioxide equilibrium tubes may be safely stored for future use—please store in bubble wrap in a safe location.

Discussion

Nitrogen oxides are formed when nitrogen and oxygen—the main components of air—combine with each other in car engines, power plants or in car exhaust (Equations 1 and 2). Nitrogen oxides are a major component of photochemical smog and air pollution.

$$N_2(g) + O_2(g) \leftrightarrows 2NO(g) \qquad \textit{Equation 1}$$

$$2NO(g) + O_2(g) \leftrightarrows 2NO_2(g) \qquad \textit{Equation 2}$$

Nitrogen dioxide (NO_2) is a toxic, reddish-brown gas with an irritating odor. It is primarily responsible for the brownish haze that hangs over many of the world's largest cities due to air pollution. Nitrogen dioxide is also quite reactive. In the presence of sunlight, for example, it undergoes a light-induced "photochemical" reaction to produce ozone (Equation 3). Therefore, high levels of nitrogen oxides in the atmosphere are associated with high ozone levels as well.

$$NO_2(g) + O_2(g) \leftrightarrows NO(g) + O_3(g) \qquad \textit{Equation 3}$$

The high reactivity of nitrogen dioxide means that it reacts even with itself—two molecules of NO_2 combine to form a "dimer," dinitrogen tetroxide, N_2O_4, which is a colorless or pale yellow gas at room temperature. Formation of N_2O_4 is a reversible reaction (Equation 4) and quickly reaches a position of equilibrium. The relative amounts of NO_2 and N_2O_4 present at equilibrium depend on pressure and temperature, according to LeChâtelier's Principle.

$$\underset{\text{red-brown}}{2NO_2(g)} \leftrightarrows \underset{\text{colorless}}{N_2O_4(g)} \qquad \textit{Equation 4}$$

The purpose of this demonstration is to study the effect of changing the temperature on the gas-phase dimerization reaction of nitrogen dioxide. LeChâtelier's Principle provides a common-sense explanation for how changing conditions affect the position of equilibrium for a reversible chemical reaction—the reaction will shift in a direction that tends to reduce the effect of the imposed change. The effect of changing the temperature thus depends on whether the reaction is exothermic or endothermic as written (see *Discussion Question* 1). Students will observe that the color of the gas in the demonstration tube increases (becomes darker brown) with increasing temperature and decreases (turns lighter brown) with decreasing temperature. Phase changes are also observed. Dinitrogen tetroxide liquefies in the vicinity of 0 °C and solidifies at approximately –10 °C.

Discussion Questions

1. Write the chemical equation for the dimerization reaction of NO_2 to give N_2O_4.

   $2NO_2(g) \leftrightarrows N_2O_4(g)$
   red-brown   colorless

2. What color change was observed when the gas was cooled? In what direction was the equilibrium shifted?

   The color changed from brown to almost colorless when it was cooled. The equilibrium was shifted in the forward direction in favor of products.

3. What color change was observed when the gas was heated? In what direction was the equilibrium shifted?

   The color changed from brown to very dark brown when it was heated. The equilibrium was shifted in the reverse direction in favor of reactants.

4. Are both reactant and product gases present in the original equilibrium mixture at room temperature? Explain.

   The reversible color changes upon heating and cooling demonstrate that both reactants and products must be present in the original equilibrium mixture at room temperature. We know there are NO_2 molecules present because of the color. We know there are N_2O_4 molecules present because the color got darker when it was heated—some of the N_2O_4 molecules present at room temperature must have dissociated upon heating.

5. Use the results of the heating and cooling experiments to predict whether the dimerization reaction of NO_2 is exothermic or endothermic. Rewrite the chemical equation for the reaction to include the heat term on the reactant or product side, as needed.

   The fact that the reaction shifted in the reverse direction upon heating means that this is the direction in which heat is absorbed. Decomposition of N_2O_4 requires energy and is endothermic, and the dimerization reaction is exothermic. Heat should appear on the produce side of Equation 4.

   $$2NO_2(g) + heat \leftrightarrows N_2O_4(g)$$

6. Use LeChâtelier's Principle to explain the effect of temperature on the gas phase equilibrium involving NO_2 and N_2O_4.

   According to LeChâtelier's Principle, increasing the temperature should shift the equilibrium in favor of the reaction that will reduce the temperature, that is, the side that will absorb the excess heat that has been added to the system. The reverse argument may be made for decreasing the temperature. In this case, the reaction should shift in favor of the side that will release some excess heat to compensate for the temperature decrease.

7. Write the equilibrium constant expression for the nitrogen oxide equilibrium. Does the value of the equilibrium constant depend on temperature? Explain.

   $$K_{eq} = \frac{[N_2O_4]}{[NO_2]^2}$$

   The value of the equilibrium constant must depend on temperature since the relative amounts of reactants and products changed when the temperature was changed even though no additional materials were added to the system.

Connecting to the National Standards

This laboratory activity relates to the following National Science Education Standards (1996):

Unifying Concepts and Processes: Grades K–12
- Evidence, models, and explanation
- Constancy, change, and measurement
- Evolution and equilibrium

Content Standards: Grades 9–12
- Content Standard A: Science as Inquiry
- Content Standard B: Physical Science, structure and properties of matter, chemical reactions, interactions of energy and matter
- Content Standard G: History and Nature of Science, nature of scientific knowledge

Flinn Scientific—Teaching Chemistry™ eLearning Video Series

A video of the *Temperature Equilibrium Tubes* activity, presented by Irwin Talesnick, is available in *LeChâtelier's Principle*, part of the Flinn Scientific—Teaching Chemistry eLearning Video Series.

Materials for *Temperature Equilibrium Tubes* are available from Flinn Scientific, Inc.

Catalog No.	Description
A0009	Acetone, 500 mL
S0065	Sodium Chloride, Rock Salt, Coarse, 1 kg
GP1040	Beaker, Borosilicate Glass, 1 L
AP1491	Dewar Flask, small, 1900-mL
AP8183	Hot Plate, Flinn, 7″ × 7″

Consult your *Flinn Scientific Catalog/Reference Manual* for current prices.