Charles's Law and Absolute Zero

Kinetic Molecular Theory and PTV

Introduction

Charles's Law describes the relationship between the temperature of a gas and its volume. In order to understand this relationship, we must imagine what happens to the particles in a gas when it is heated or cooled. The temperature of a gas measures the average kinetic energy of the gas particles—how fast they are moving. When a gas is heated, the kinetic energy of the particles increases and they move faster. When a gas is cooled, the kinetic energy of the particles decreases and they move slower. Is there a lower limit to the temperature scale at which the particles stop moving altogether and their kinetic energy is zero? What would happen to the volume of a gas at this minimum temperature?

Concepts

- Temperature
- Absolute zero
- Charles's law
- Kinetic-molecular theory

Background

The purpose of this activity is to carry out a modern version of classic experiments relating the volume and temperature of a gas. The demonstration will be carried out using gases trapped inside sealed syringes. The syringes will be placed in water baths ranging in temperature from –15 °C to 80 °C. The volume of each gas will be measured at five different temperatures to test whether the Charles's Law relationship is valid for different gases. The data will be plotted on a graph and then extrapolated backwards to estimate how low a temperature would be needed to reduce the volume of a gas to zero, that is, to reach absolute zero.

Materials

Gas sources (air, hydrogen, helium, nitrogen, etc.), 2
Ice
Salt (sodium chloride)
Silicone grease lubricant
Water
Beakers, 400-mL, 5
Hot plate
Scoop (large spatula)
Syringe, large, 30-mL
Syringe, small, 10-mL
Syringe tip caps, 2
Thermometer
Wooden splint or tongue depressor

Safety Precautions

Handle pressurized gas sources (lecture bottles or gas cylinders) with caution. If working with hydrogen, avoid contact of the gas with any source of ignition (flames or sparkers) in the lab. Wear gloves to apply silicone grease. Always wear eye protection (safety glasses or chemical splash goggles) whenever working with chemicals, glassware, or heat. Wash hands thoroughly with soap and water before leaving the lab. Please review current Material Safety Data Sheets for additional safety, handling, and disposal information.

Procedure

1. Obtain five 400-mL beakers and label them #1–5. Prepare water baths at different temperatures as follows:
    - Add crushed ice and water (total volume 250 mL), followed by 5–6 scoop-fulls of salt to beaker #1 to prepare a bath at a temperature between –10 °C and –15 °C.
    - Add crushed ice and water to beaker #2 to prepare a 0 °C-bath.
    - Add 250 mL of room temperature water to beaker #3 to prepare a 20 °C-bath.
    - Add 250 mL of hot running water to beaker #4 to prepare a 40–50 °C-bath.

- Add 250 mL of water to beaker #5 and heat it on a hot plate at a medium setting to prepare a hot water bath at about 80 °C.

2. Add hot water or ice as needed during the course of the experiment to maintain the temperature of each bath within ±5 °C of the desired temperature.
3. Obtain one small and one large syringe. Lubricate the plunger of each syringe with silicone grease. Wearing gloves, apply a dab of grease to the black rubber gasket and use a wooden splint or tongue dispenser to spread a thin layer of grease over the surface of the gasket.
4. Fill one syringe about ½-full with air and seal the syringe with a syringe tip cap.
5. Fill the second syringe with a different gas. Attach the syringe tip to a gas source, turn on the gas source, and pull on the plunger to fill the syringe completely with the gas. Disconnect the syringe from the gas source, push on the syringe to expel the gas, then reattach the syringe to the gas source and fill the syringe about ½-full again. Seal the syringe with a syringe tip cap and record the identity of the gas (hydrogen, helium, etc.).
6. Measure and record the temperature of the coldest water bath (beaker #1). Place the first syringe in the bath and submerge the syringe just up to the bottom of the plunger (see Figure 1). Hold it there for two minutes, then quickly push down on the plunger once and release it.
7. Measure and record the volume when the plunger stops moving. *Note:* Keep the syringe in the water bath the entire time.
8. Remove the syringe from the first bath and place it in the second temperature bath. Repeat steps 7 and 8 to measure the new temperature and volume of the gas.
9. Repeat steps 7 and 8 at the remaining water-bath temperatures to obtain a total of five different temperature–pressure readings.
10. Repeat steps 7–10 with the second syringe filled with a different gas.

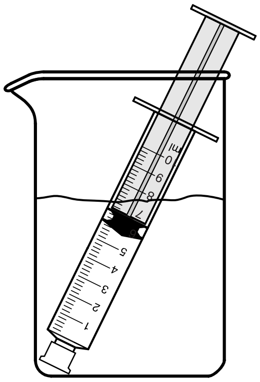


Figure 1.

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 syringes should be taken apart and wiped clean with a paper towel to remove the silicone grease. Wash the syringes with mild, soapy water and store the syringes for future use.

Tips

- Silicone grease was found to be the most effective syringe lubricant for different gases across the temperature range recommended in this experiment. Although petroleum jelly worked well with an air-filled syringe, it could not be used with other gases, including hydrogen, helium, and nitrogen, at temperatures above about 50 °C (the plunger would get stuck).
- Five temperature points are recommended in the *Procedure* section. Adding a below zero water bath (–15 °C) gives a more accurate estimate of absolute zero than adding a boiling water bath.
- The reliability and reproducibility of the method were tested for five different gases (air, nitrogen, hydrogen, helium, and carbon dioxide) in three different size syringes (10-, 30-, and 60-mL). The results were consistent for different gases and different sample sizes. The *Sample Data* section summarizes the results obtained with air and hydrogen in 10- and 30-mL syringes. In general, 60-mL syringes did not give accurate results.
- This demonstration can be used as a lead-in for a guided inquiry experiment. Testing different gases shows that the ideal gas behavior implied by the gas laws also describes "real" gases under a variety of conditions. By making available a variety of gases for different student groups to test, teachers can encourage a collaborative learning environment. Another good question for students to investigate would be how the size of the syringe and volume of gas affect the reliability of the results. (In general, larger volumes take longer to cool and give less precise results.)
- Gases are available in convenient lecture bottle and refillable cylinder sizes. Consult your current *Flinn Scientific Catalog/Reference Manual* for a complete listing of gas sources and supplies, including regulator valves. Be creative and flexible in

locating alternative gas sources for this experiment. Helium-filled Mylar™ balloons, for instance, are inexpensive sources of helium. Gas outlets in the lab may be used as sources of methane (natural gas). Exercise caution when working with natural gas to prevent accidental exposure to flames or other sources of ignition.

- Both Jacques Charles and Joseph Gay-Lussac were at least partially inspired by their interests in hot-air ballooning to study the properties of gases. If it worked for them, it may work for your students as well! Inspire students to learn more about the properties of gases with the hot-air balloon activity kit "Up, Up, and Away" (Flinn Catalog No. AP6310). The kit contains enough materials for each pair of students to construct and launch their own giant hot-air balloon.
- Why did it take more than 40 years to go from Charles's Law (Gay-Lussac's Law in Europe) to a definition and value for absolute zero? The answer has to do with the lack of a functional definition of heat in the early 19th century. Thomson's groundbreaking paper on the value of absolute zero followed immediately upon Joule's famous experiment demonstrating the mechanical equivalent of heat energy. Thomson estimated the value of absolute zero based on the coefficient of expansion of gases (the relative increase in the volume of a gas per degree Celsius). Although Gay-Lussac had previously determined the coefficient of expansion of gases, he lacked a theoretical basis for proposing the existence of absolute zero.
- In their quest to reach absolute zero, scientists have come very, very close, but have never reached true absolute zero. It can be argued that absolute zero is theoretically impossible because in order to cool something, heat must flow out of a system at a higher temperature to one at a lower temperature. Since there cannot be a reservoir below absolute zero, heat cannot flow out of a system to reach absolute zero. Physicists say that absolute zero is impossible because the third law of thermodynamics says so and because it violates the principles of quantum mechanics!

Discussion

Charles's Law, which describes how the volume of a gas changes as it is heated or cooled, was inspired by the first sensational flight in the history of hot-air ballooning. The world's first, manned, hot-air balloon flight took place in France in 1783. A few months later, Jacques Alexandre César Charles, professor of physics at the Sorbonne University in France, made the first flight in a lighter-than-air (hydrogen) balloon, climbing to a height of 9000 meters. Motivated by twin interests in science and ballooning, Charles not only made more flights, he also studied the factors that influence the flight of a hot air balloon. A hot air balloon works on the principle that the volume of a gas expands when heated. When the gas inside a balloon is heated, the gas expands and the hot air balloon becomes less dense than the air it displaces, causing the balloon to rise and float in the atmosphere.

Charles investigated this principle in the laboratory by measuring the increase in volume of a fixed amount of air when it was heated at a constant pressure. Charles's unpublished work was taken up by another French scientist and balloon enthusiast, Joseph-Louis Gay-Lussac, who studied the expansion of oxygen, hydrogen, nitrogen, carbon dioxide, nitrous oxide, and ammonia. In 1802 Gay-Lussac concluded that all of these gases expanded equally when heated from 0 to 100 °C—the volume of a gas is proportional to its temperature and does not depend on the nature of the gas.

This conclusion led to the development of more precise "air thermometers" for measuring temperature. Although very precise, air thermometers were still arbitrary—there was no absolute basis for any of the numbers on the scale. In 1848 the British mathematician William Thomson (knighted Lord Kelvin in 1866) proposed an absolute temperature scale based on the assumption that there must be a lower limit to temperature. He wrote:

> "…*Infinite cold must correspond to a finite number of degrees of the air thermometer below zero, since if we push the strict principle of graduation … sufficiently far, we should arrive at a point corresponding to the volume of air being reduced to nothing…*"

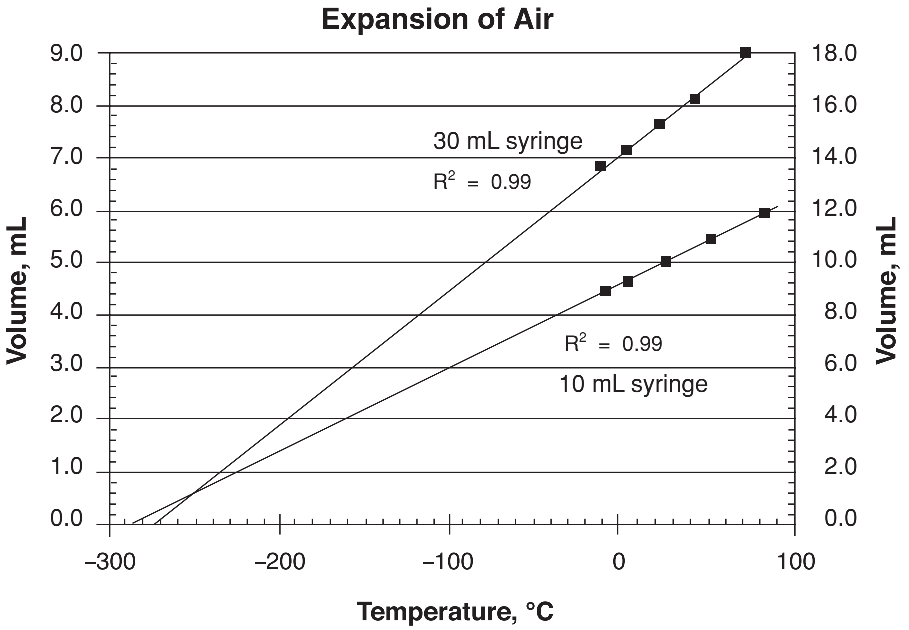
Thomson estimated a value for the "infinite cold" temperature on the Celsius scale. This temperature is known today as absolute zero and the temperature scale is called the Kelvin or absolute temperature scale. The units on this scale corresponding to the degree units on the Celsius scale are called *kelvins* (abbreviated K) in honor of Lord Kelvin.

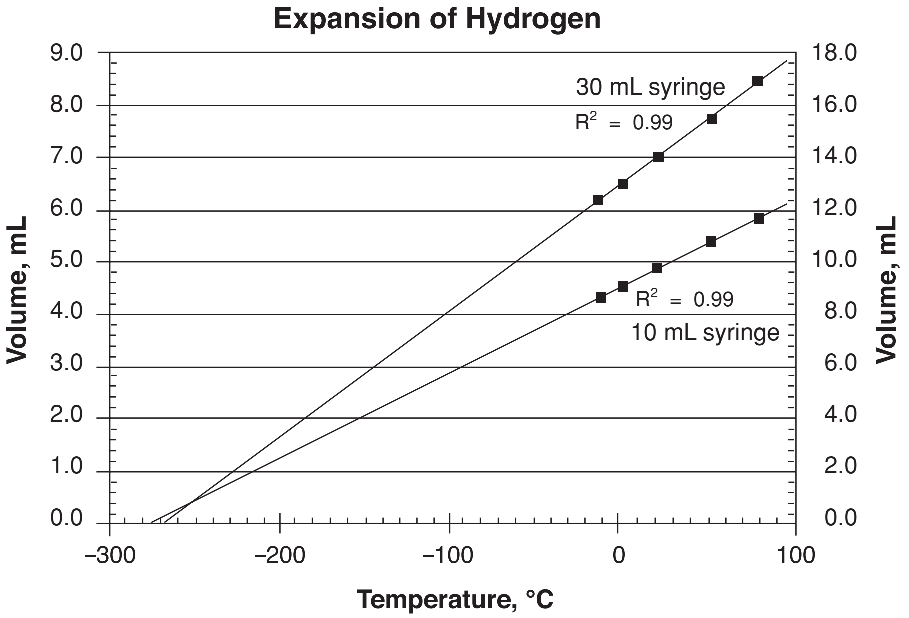
Charles's Law describes how gases behave when heated, but does not explain why. The best model for explaining the behavior of gases is called the kinetic-molecular theory (KMT). According to this model, the average kinetic energy of a gas depends only on the temperature, and pressure, defined as force per unit area, results from the collision of gas particles with the walls of the container. This model can be used to explain how and why the volume of a gas in a *flexible* container (such as a syringe or a balloon) changes when the gas is heated. When a gas is heated in a flexible or elastic container, the volume will tend to expand so that the pressure inside the container is the same as the pressure of the surrounding air outside the container. Heating the gas increases the average kinetic energy of the gas particles and the particles move faster. As the particles move faster in the same size container, they will collide more often and with more force against the walls of the container. If the walls of the container are flexible, this additional force pushes out or stretches the container.

Sample Data and Results

10 mL Syringe		**10 mL Syringe**	
Identity of Gas	*Air*	**Identity of Gas**	*Hydrogen*
Temperature (°C)	**Volume (mL)**	**Temperature (°C)**	**Volume (mL)**
–15	4.4	–14	4.3
0	4.6	0	4.5
21	5.0	21	4.8
48	5.4	52	5.4
80	5.9	80	5.8

30 mL Syringe		**30 mL Syringe**	
Identity of Gas	*Air*	**Identity of Gas**	*Hydrogen*
Temperature (°C)	**Volume (mL)**	**Temperature (°C)**	**Volume (mL)**
–14	13.6	–14	12.5
0	14.1	1	13.0
20	15.1	21	14.0
40	16.0	52	15.5
71	18.1	80	17.0





Very small changes in the best-fit straight line as it passes through the data points lead to very large changes in where the line crosses the *x*-axis. The lines in the sample graphs were obtained by linear regression. The following values of absolute zero were extrapolated from the data.

- Air, 10-mL syringe: –285 °C
- Air, 30-mL syringe: –274 °C
- Hydrogen, 10-mL syringe, –275 °C
- Hydrogen, 30-mL syringe, –268 °C
- Average value of absolute zero: –276 °C

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
Content Standards: Grades 9–12
Content Standard A: Science as Inquiry
Content Standard B: Physical Science, structure and properties of matter, motions and forces, interactions of energy and matter
Content Standard G: History and Nature of Science, science as a human endeavor, nature of scientific knowledge, historical perspectives

Flinn Scientific—Teaching Chemistry™ eLearning Video Series

A video of the *Charles's Law and Absolute Zero* activity, presented by Irene Cesa, is available in *Kinetic Molecular Theory and PTV*, part of the Flinn Scientific—Teaching Chemistry eLearning Video Series.

Materials for *Charles's Law and Absolute Zero* are available from Flinn Scientific, Inc.

Catalog No.	Description
LB1015	Hydrogen Lecture Bottle
AP1095	Grease
AP1730	Syringe, without Needle, 10 mL
AP1732	Syringe, without Needle, 35 mL
AP6049	Thermometer, Digital
AP7234	Hot Plate, Flinn, 7"× 7"
LB1051	Lecture Bottle Control Valve, Brass
AP8958	Syringe Tip Cap, Pkg/10

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