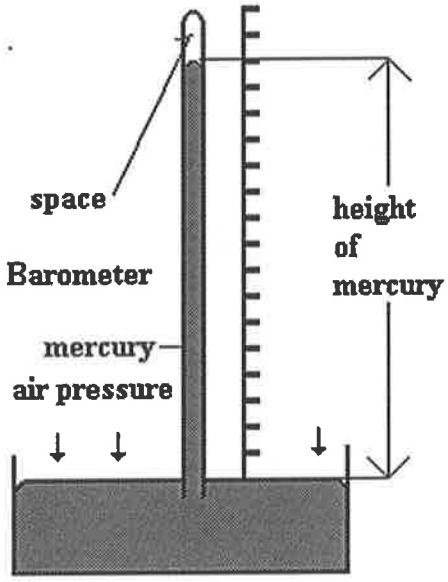
KINGSBOROUGH COMMUNITY COLLEGE
THE CITY UNIVERSITY OF NEW YORK

Thall's History of Gas Laws

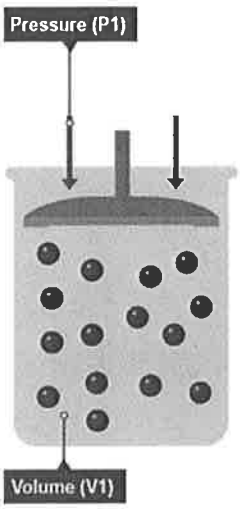
The gas laws started to evolve in 1643 with the invention of the barometer and continued until 1873 with the van der Waals equation. Note that this is well before the birth of the modern atomic theory. The gas laws led to numerous concepts including the mole, temperature, formula weight, absolute zero, kinetic energy, and stoichiometric coefficients. This brief history highlights some of the early pioneers.

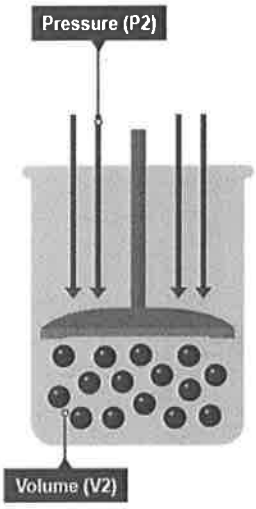
Barometer



Evangelisto Torricelli (1608-1647)
Torricelli served as Galileo's secretary (1641-1642) and succeeded him as court mathematician to Grand Duke Ferdinando II. Torricelli used mercury to make the first barometer in 1643. Mercury is more than 13 times as dense as water; a water barometer would require a tube more than 30 feet long. Under standard conditions at sea level, the height will be 29.92 inch or 760 millimeters. The invention of the barometer allowed Boyle to discover the relationship between Pressure and volume. (Torricelli letter to Michelangelo concerning the Barometer)

Boyle's Law: $P_1V_1=P_2V_2$



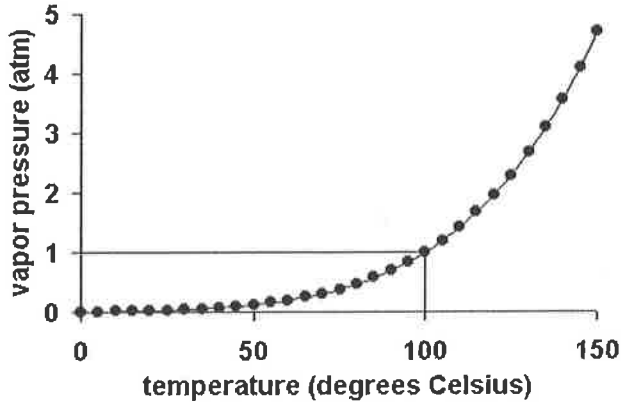


Robert Boyle (1627-1691)

Boyle had the good fortune to have Robert Hooke as an assistant and together they made an air pump. Recognizing its scientific possibilities, Boyle conducted pioneering experiments in studying the role of air in combustion, respiration, and the transmission of sound. In 1662, Boyle published what is now known as Boyle's law: At constant temperature the volume of a gas is inversely proportional to the pressure.

Boyle was aware that a gas expands when heated but no temperature scale existed and he could not determine the relationship between "hotness" and, volume.

Amontons' Law: $P_1T_2=P_2T_1$

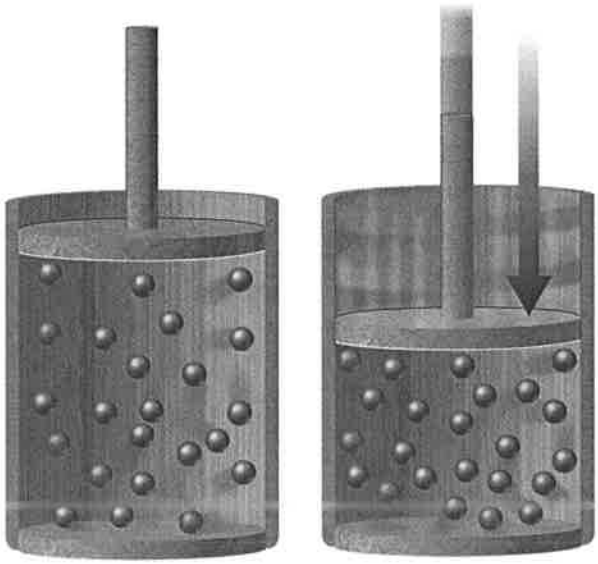


Guillaume Amontons (1663-1705)

Amontons developed the air thermometer--it relied on increase in volume of a gas with temperature rather than the increase in volume of a liquid. Amontons failed to discover Charles'

law for the same reason as Boyle: a temperature scale did not exist. Using the air thermometer, Amontons (1702) devised a method to measure change in temperature in terms of a proportional change in pressure. Although Amontons' law became the most obscure of the gas laws, it was this work that eventually led to the concept of absolute zero in the 19th century.
As a consequence of becoming deaf as a young boy, Amontons worked on inventions to benefit the deaf. One of his inventions, the first telegraph, relied on a telescope, light, and several stations to transmit information over large distances. Although not adopted in Amontons lifetime, the ideas were later refined and put into use.

Kinetic Theory of Gases



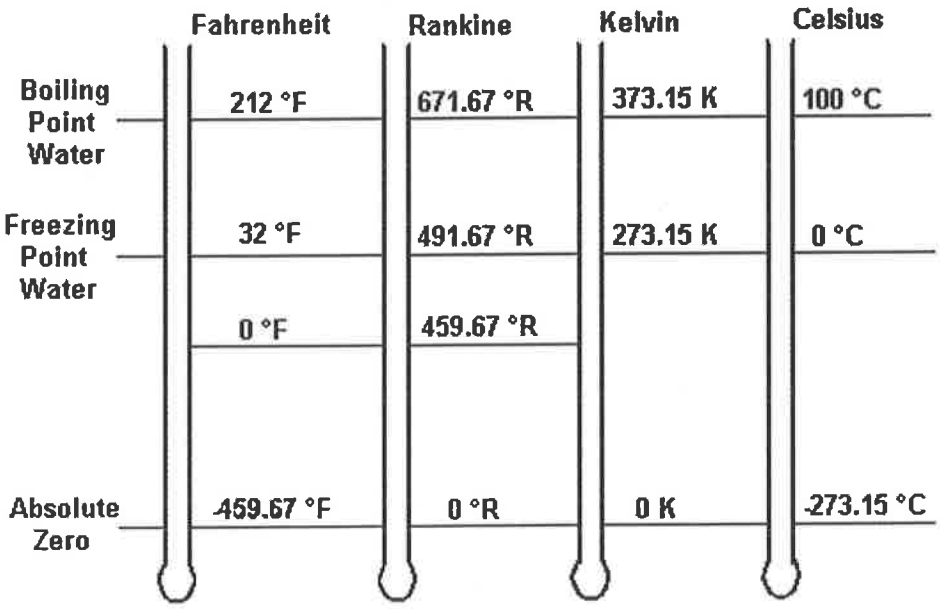
Gas

Daniel Bernoulli (1700-1782)

Bernoulli studied medicine at the insistence of his father Johann Bernoulli, chair of mathematics in Basel Switzerland. However the younger Bernoulli became interested in his father's theories of kinetic energy and even applied these theories to his doctoral dissertation on the mechanics of breathing. While practicing medicine in Venice, Bernoulli published his first mathematical work consisting of four separate parts: (1) Probability, (2) flow of water from a hole in a container, (3) the Riccati differential equation, and (4) a geometry question concerning figures bounded by two arcs of a circle. These papers won him a position at the influential Academy of Sciences in St. Petersburg, Russia. At the academy Bernoulli lectured in medicine, mechanics, and physics. He developed what is now called Bemoulli's principle: The pressure in a fluid decreases as its velocity increases.

The modern kinetic molecular theory of gases essentially started with Bernoulli's suggestion in 1734 that the pressure exerted by a gas on the walls of its container is the sum of the many collisions by individual molecules, all moving independently of each other. Bernoulli derived the basic laws for the theory of gases and gave, although not in full detail, the equation of state discovered by van der Waals a century later.

Temperature Scale



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Measurement of temperature has developed relatively recently in human history. The invention of the thermometer is generally credited to Galileo who developed the first known thermometer (1592) based on the expansion/contraction of air. German physicist Fahrenheit made a mercury thermometer (I714) ranging from the freezing of water (32°) to body temperature (96°). Swedish astronomer Celsius (I742) devised a scale ranging from the boiling of water (0°) to the freezing of water (100°)--this inverted scale (centigrade) gained widespread use and in 1948 the name was changed to Celsius. In 1848 British physicist William Thomson (Lord Kelvin) proposed a system using degree Celsius but starting at zero Kelvin (-273°C).

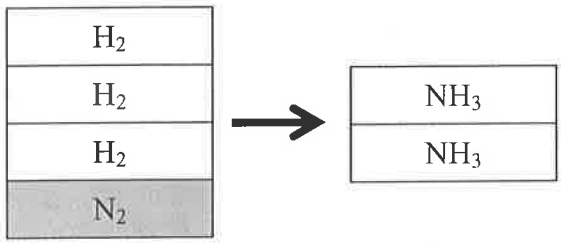
Charles' Law: $V_1T_2=V_2T_1$

Jacques Charles (1746-1823)

The physical principle known as Charles' Law states that the volume equals a constant value multiplied by its temperature as measured on scale. The law's name honors the pioneer balloonist Jacques Charles, who in 1787 did experiments on how the volume of gases depended on temperature.

The irony is that Charles never published the work for which he is remembered, nor was he the first or last to make this discovery. In fact, Amontons had done the same sorts of experiments 100 years earlier, and it was Gay-Lussac in 1808 who made definitive measurements and published results showing that every gas he tested obeyed this generalization.

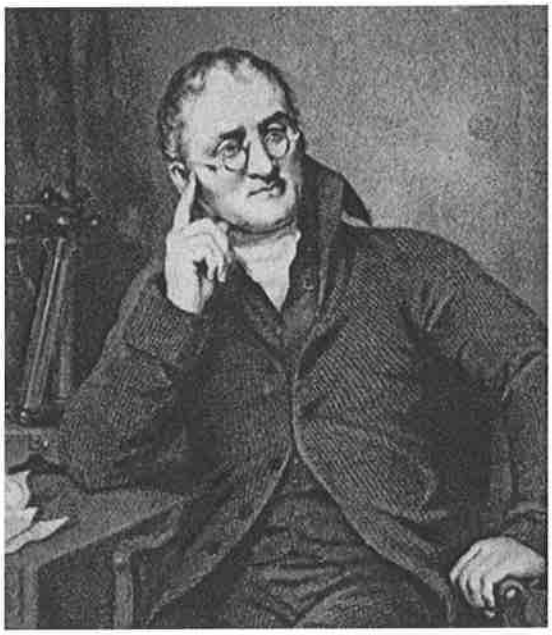
Law of Combining Volumes



Joseph Gay-Lussac (1778-1850)

Gay-Lussac carefully investigated the ratio of the volume of hydrogen gas that combined with a given volume of oxygen gas to form water. He found the oxygen could combine with exactly twice its own volume of hydrogen. There were similar simple volumetric ratios for other reactions between gases and if the product of the reaction was also a gas, it filled a volume simply related to those of the combining gases.
Gay-Lussac combined research with his passion of hot air balloons. Because nitrogen is lighter than oxygen, Gay-Lussac reasoned there might be proportionately less oxygen in the air at higher elevations. To find out, in 1802 he went up in a balloon to 23,000 feet (a record for 50 years). He found the proportions nearly the same.

Law of Partial Pressures: $P_T=P_1+P_2+P_3+\cdots$



John Dalton (1766-1844)

Dalton's law of partial pressures was stated by John Dalton in 1801: The total pressure of a mixture of gases is equal to the sum of the partial pressures of the individual component gases. The partial pressure is the pressure that each gas would exert if it alone occupied the volume of the mixture at the same temperature.

Avogadro's Principle

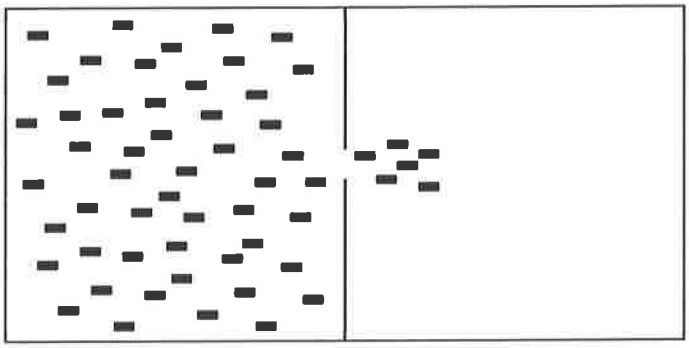
At 0°C and 1 atm, 22.4 L contain 1 mol of any gas

H_2	He	N_2	O_2	CO_2	SO_2

Amadeo Avogadro (1766-1856)

After practicing law for three years, Avogadro began to study mathematics and physics. Eventually he was appointed Professor of Natural Philosophy at the College of Vercelli. Based on the work of Gay-Lussac, all gases when subjected to an equal rise in temperature expand by the same amount, Avogadro published an article (1811) stating that at the same temperature and pressure, equal volumes of different gases contain the same number of molecules. The science community was not ready to accept such a radical idea and Avogadro's Principle went ignored for the next 50 years. Avogadro's work was finally recognized when countryman Stanisalo Cannizaro presented the work at a Conference in 1860. Today, one mole (6.022E23) is called Avogadro's number. At the time Avogadro's principle was becoming acceptable, Bernoulli's 1738 kinetic model of tiny gas molecules moving about in otherwise empty Space was also reexamined; our modern view of gases began to emerge in 1860.

Graham's Law of Effusion: $u_1/u_2=(m_2/m_1)^{1/2}$

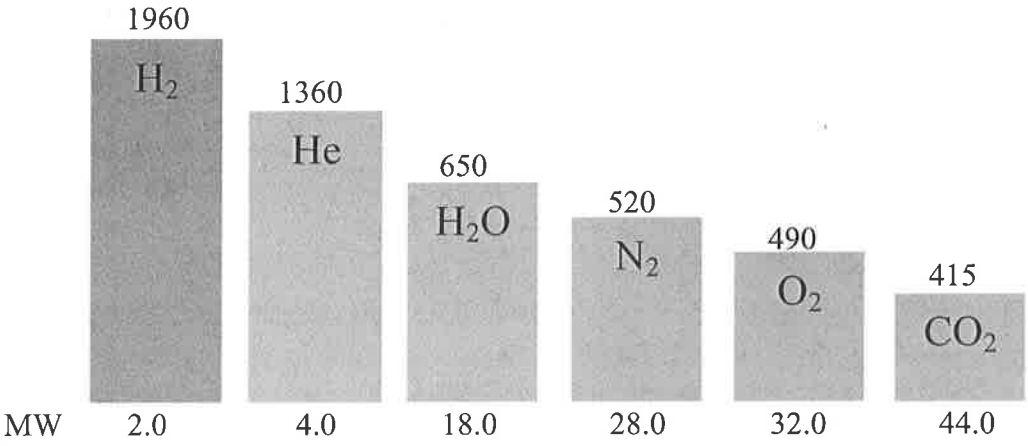


Thomas Graham (1805-1869)

Graham was professor of chemistry at University College in London and later became Master of the Mint. He is best known for Graham's law (1846) which states that the rate of effusion of a gas is inversely proportional to the square root of its molecular weight. Graham also devised the technique known as dialysis to separate colloids from crystalloids and coined many of the terms used in colloid chemistry.

Molecular Speed: $u=(3RT/M)^{1/2}$

Average speeds (m/s) at 25°C



James Clerk Maxwell (1831-1879)

Maxwell treated gases statistically (1866) and formulated what has-become known as the root-mean-square molecular equation ($u = [3RT/M]^{1/2}$. This represents a relationship between molecular mass, average speed, and temperature (R is the familiar gas constant). Because two gases with two different masses must have the same average kinetic energy at the same temperature, the heavier gas molecules must possess lower average speed. On another front, Maxwell's mathematical equations expressing the behavior of electric and magnetic fields are considered one of great achievements of the 19th century.

Your instructor will now have you read the pressures at a set of given volumes. Please fill in the data in the table below.

Table 6.1 Data on Boyle's Law

Volume (cc)	Pressure (lb/sq in)	Constant (cc-lb/sq in)
32		
30		
28		
26		
24		
22		
20		

Average value of the constant _____

QUESTIONS

1. What is the pressure reading at the start of the experiment?

2. Describe your physical reactions after each successive volume addition.

3. After your last volume introduction, release the plunger and describe what has happened.

EXPERIMENTAL PROCEDURE

For the most part, this experiment will be a demonstration-discussion. Your instructor will guide you through a series of demonstrations, and your job will be to apply these phenomena to functions within the body.

1. In the first case, you will be shown an empty beverage can and asked what is in it? Is it empty? Next, you will be asked, how does it maintain its shape? On a microscopic level, describe what is going on inside of the can. The instructor will add a few milliliters of water to the can, and using a pair of tongs, will proceed to heat the can. Describe what you think is occurring inside of the can. Finally, the can will be placed into a container of water. Again, describe what has happened.

   Where might such a similar event take place within the body?

2. Pressure-Volume relationship

As you have read in preparing for this lab, the gas laws are very important in aiding us in our everyday lives. Today's lab will give you some insight into what is involved with the various gas laws.

Through guided inquiry, you'll find that the hands-on apparatuses will make things more understandable. The Boyle's law apparatus will help you understand the relationship between the pressure and volume of a gas. Boyle's law states that the pressure on a gas will be inversely proportional to its volume. i.e. when one variable goes up, the other goes down. Mathematically speaking.

$$\text{VOLUME} \propto 1/\text{PRESSURE}$$

Where $\propto$ = is the symbol for proportionality

Since may be a bit "upsetting" to some of us, we can get rid of the proportion sign by introducing a constant.

So, VOLUME = k / Pressure, and if we want to know what the constant k is, we rearrange to:

$$\text{VOLUME} \times \text{PRESSURE} = \text{CONSTANT (k)}$$

$$\text{or } VP = k; \qquad k \text{ is the proportionality constant}$$

Your job is to find that constant by experiment.

Charles' Law – in 1787, the French physicist, reported from his experiments that *at constant volume, the pressure exerted by a confined gas is proportional to its absolute temperature.* In 1802, **Gay-Lussac**, restated Charles' Law in the form that is used today, namely, that *at constant pressure, the volume of a confined gas is proportional to its absolute temperature (T).*

3. Volume-Temperature:

Observe an "air" thermometer, which is a capillary tube that is sealed at one end and has a drop of mercury (Hg) in it. The position of the Hg measures the volume of air trapped in the closed end of the tube.

In this demonstration we are going to construct a "crude" thermometer from known temperature extremes: boiling water at 100°C, and an ice-water mixture at 0°C. The task this time is to determine the room temperature, on the absolute scale (100°C – 373 K; 0°C – 273 K).

1. Measure the distance from the closed end of the tube to the rubber ring _____ cm

CAUTION: Do not "shake" the drop of mercury

Now, place the tube, sealed end first, into an ice bath.

2. Measure the distance the drop of Hg has moved _____ cm

Repeat, this time placing the air thermometer in hot water.

3. Measure the distance the drop of Hg has moved _____ cm

How many centimeters between T (room) and T (ice) _____ cm

How many centimeters between T (room) and T (boiling) _____ cm

Total number of centimeters between T (ice) and T (boiling) _____ cm

Total number of degrees between T (ice) and T (boiling) _____ cm

Divide the total number of degrees by the total number of centimeters _____ K/cm

What is the approximate temperature? _____ K

The instructor will demonstrate the operation and adjustments of a Bunsen burner. This is names for German chemist, Robert Wilhelm von Bunsen (1811-1899). Bunsen had also devised many other pieces of apparatus, such as the grease-spot photometer, the Bunsen electric cell, and the filter pump. Working together with Kirchhoff and Roscoe, Bunsen is also credited with the discovery that each chemical element produces a unique emission spectrum. That discovery laid the foundation for spectrum analysis (compare Experiment on spectroscopy). Through his studies of the emission spectra, Bunsen discovered the elements cesium and rubidium.

The burner flame →

4 Law of Pressure – Temperature: The apparatus is shown in the figure 6.4 below. This set-up keeps the volume of air in the system constant. A change in the pressure of the gas will cause the liquid in the capillary to rise or fall.

A. In this demonstration the flask is *gently heated*, with a Bunsen burner. Note the change in the level of the liquid.

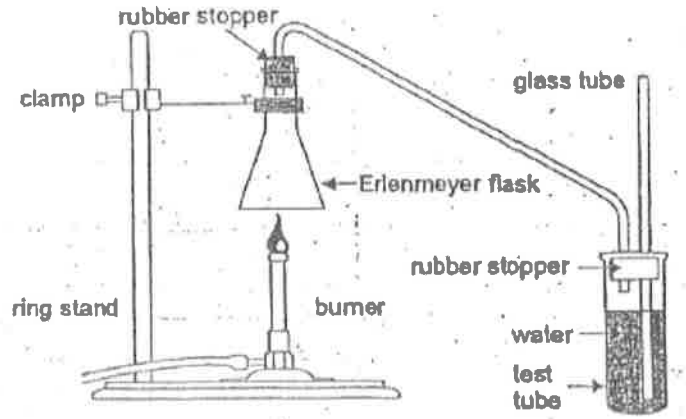


Figure 6.4

i. How does the pressure of a gas change with increasing temperature?

ii. Describe what might occur if the burner is left under the flask.

iii. Which physiological phenomenon, in the body, follows this mechanism?

B. Allow the flask to cool to room temperature or blow on it to cool it, and note what happens.

i. How does the pressure of a gas change with decreasing temperature?

ii. In patient / client care, how might this knowledge be put to good use?

Questions and Discussion of Applications

Answer the following questions to summarize the properties of gases:

1. At constant temperature, as the pressure increases, the volume _____
2. At constant temperature, as the pressure decreases, the volume _____
3. At constant volume, as the temperature increases, the pressure _____
4. At constant volume, as the temperature decreases, the pressure _____
5. At constant pressure, as the temperature increases, the volume _____
6. At constant pressure, as the temperature decreases, the volume _____
7. Why do you suppose they only partially fill high altitude balloons before they release them? (HINT: The external or *atmospheric* pressure decreases as altitude increases) _____

_____

8. Many treatments, such as oxygen therapy, artificial pneumothorax, and surgical pneumothorax, depend on the behavior of gases described by Boyle's law and Charles' law. Artificial pneumothorax depends on the existence of a small space between the lungs and the walls of the chest, called the *intrapleural space* or the *pleural cavity.* The pressure in this space is normally *less* than that of the atmosphere. If the chest wall or the lungs were punctures, air would enter the intrapleural space; the pressure would increase, and the increased pressure would cause the lungs to collapse.

   a. Artificial pneumothorax is induced by surgical opening to permit the resting of a diseased lung in pulmonary tuberculosis. Which gas law applies in the case of artificial pneumothorax? (Look up *pneumothorax* in the glossary of your physics text) _____

   b. In your own words explain what you mean by *pneumothorax.*

Answer the following gas law questions.

1) According to the kinetic theory of gases, which assumption is correct?

A) Energy may be transferred between colliding particles.
B) The volume of gas particles prevents random motion.
C) Gas particles strongly attract each other.
D) Gas particles travel in curved paths.

2) The average kinetic energy of the molecules of an ideal gas is directly proportional to the

A) pressure at standard temperature
B) temperature measured on the Kelvin scale
C) number of moles present
D) volume occupied by individual gas molecules

3) A flask containing molecules of gas A and a separate flask containing the molecules of gas B are both at the same temperature. Gases A and B must have equal

A) pressures
B) average
C) masses
D) volumes

4) Which change must result in an increase the average kinetic energy of the molecules of a sample of $N_2(g)$?

A) The temperature changes from 20°C to 30°C.
B) The density changes from 2.0g/ℓ to 2.5g/ℓ.
C) The pressure changes from 0.5 atmosphere to 1 atmosphere.
D) The volume changes from 1 liter to 2 liters.

5) As the pressure on a sample of a gas increases at constant temperature, the volume of the gas

A) remains the same
B) decreases
C) increases

6) As the pressure of a gas at 101.3 Kpa is changed to 50.65 kPa at constant temperature, the volume of the gas

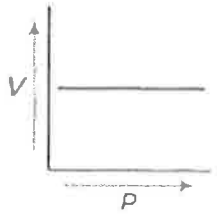
A) increases
B) remains the same
C) decreases

7) As the pressure on a given sample of a gas increases at constant temperature, the mass of the sample

A) remains the same
B) increases
C) decreases

8) Which graph *best* represents how the volume of a given mass of a gas varies with the pressure exerted on it at constant temperature?

A)



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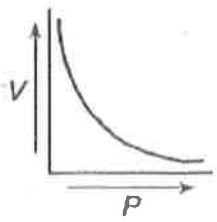

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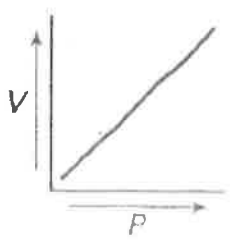

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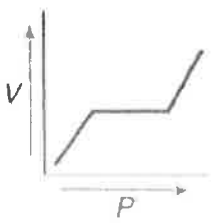
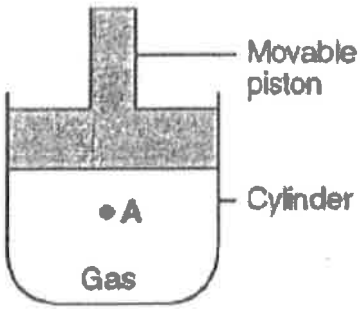


9) The diagram represents as a gas confined in a cylinder fitted with a movable piston



As the piston moves toward point A at constant temperature, which relationship involving pressure (P) and volume (V) is correct?

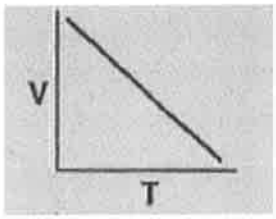
A) $\frac{P}{V} = k$ B) $P - V = k$ C) $P + V = k$ D) $P \times V = k$

10) The volume of a given mass of an ideal gas at constant pressure is
A) inversely proportional to the Celsius temperature
B) inversely proportional to the Kelvin temperature
C) directly proportional to the Kelvin temperature
D) directly proportional to the Celsius temperature

11) As the temperature of a sample of a gas increases at constant pressure, the volume of a gas (V) and its absolute temperature (T)?

A) remains the same B) increases C) decreases

12) At constant pressure, which graph shows the correct relationship between the volume of a gas (V) and its absolute temperature (T)?

A)


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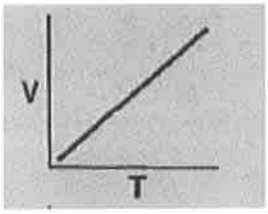

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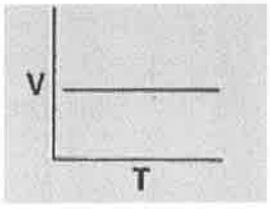

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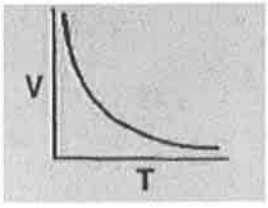

13) As gas occupies a volume of 30 milliliters at 273 K. If the temperature is increased to 364 K while the pressure remains constant, what will be the volume of the gas?

A) 40 mL B) 20 mL C) 30 mL D) 60 mL

14) A sample of gas is at STP. As the pressure decreases and the temperature increases, the volume of gas

A) remains the same B) increases C) decreases

15) A sample of gas A was stored in a container at a temperature of 50oC and a pressure of 0.50 atmosphere. Compared to a sample of gas B at STP, gas A had a

A) higher temperature and a lower pressure
B) lower temperature and a higher pressure
C) lower temperature and a lower pressure
D) higher temperature and a higher pressure

16) A gas has a volume of 2 liters at 323 K and 3 atmospheres. When its temperature is changed to 273 K and the pressure is changed to 1 atmosphere, the new volume of the gas would be equal to

A) $2\text{ L} \times \frac{273\text{ K}}{323\text{ K}} \times \frac{3\text{ atm}}{1\text{ atm}}$

C) $2\text{ L} \times \frac{323\text{ K}}{273\text{ K}} \times \frac{3\text{ atm}}{1\text{ atm}}$

B) $2\text{ L} \times \frac{273\text{ K}}{323\text{ K}} \times \frac{1\text{ atm}}{3\text{ atm}}$

D) $2\text{ L} \times \frac{323\text{ K}}{273\text{ K}} \times \frac{1\text{ atm}}{3\text{ atm}}$

17) A gas sample has a volume of 25.0 milliliters at a temperature of 75.0o and 1.00 atmosphere of pressure. What will be the final temperature of the gas (in degrees Kelvin) if the volume increases to 50.0 milliliters and the pressure remains constant? [*Write the correct formula. Show all work. Indicate the correct answer with an appropriate unit.]*

18) A sample of gas occupies 15.0 liters at 4.00 atmospheres and 300 K. What is the new volume of the gas if pressure is decreased to 2.00 atmosphere and temperature is increased to 400 K? [*Write the correct formula. Show all work. Indicate the correct answer with an appropriate unit.*]