

BOYLE'S AND CHARLES' LAWS

OBJECT: To study Boyle's law and Charles' law, as applied to air at moderate temperatures and pressures.

METHOD: To study Boyle's law a fixed mass of air confined in a glass tube is kept at room temperature and subjected to various pressures, ranging from half to double atmospheric pressure. A series of corresponding pressures and volumes are observed and Boyle's law is checked by noting the constancy of their products. The data are plotted in several graphical forms the interpretation of which also indicates the validity of Boyle's law. Charles' law for the expansion of gases is studied by the use of a simple form of constant-volume air thermometer. A fixed volume of dry air is subjected to certain measured temperatures and the corresponding pressures observed. From the resultant pressure-temperature curve the temperature coefficient of pressure increase at constant volume is determined. By extrapolating this curve the value of "absolute zero" is approximately measured.

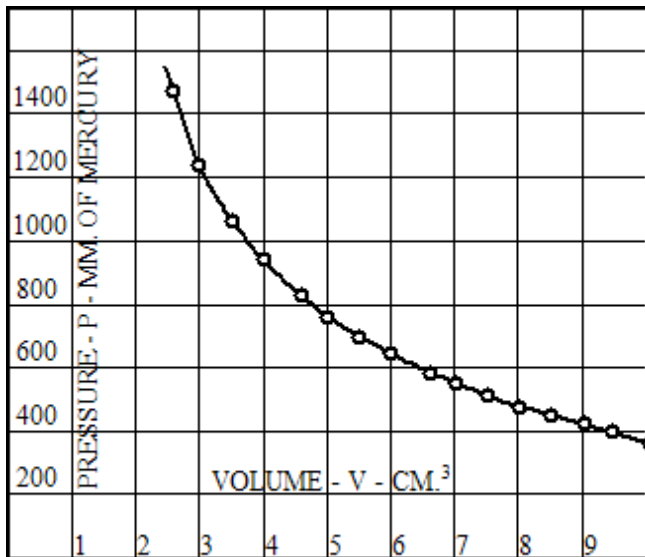


Fig. 1. Curve showing the variation of the volume of a gas at constant temperature as a function of the pressure.

THEORY:

Boyle's Law: The relation existing between the pressure exerted by a confined gas and its volume is given by what is usually known as Boyle's law, namely: *The temperature remaining constant, the volume V occupied by a given mass of gas is inversely proportional to the pressure p to which it is subjected.* In symbols

$$V \propto \frac{1}{P} \quad \text{or} \quad V = k \times \frac{1}{P}$$

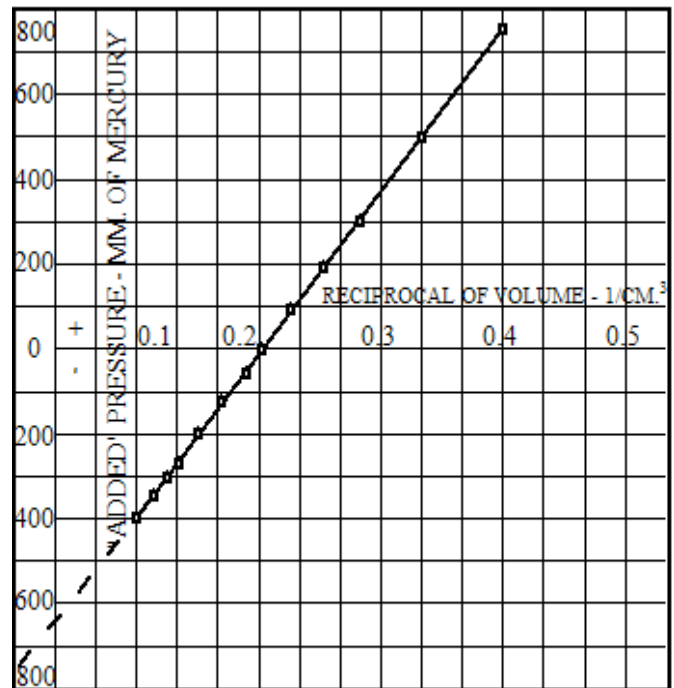


Fig. 2. Curve showing the variation of the reciprocal of the volume of a fixed mass of gas at constant temperature, as a function of the pressure above and below the atmospheric pressure.

whence

$$PV = k \tag{1}$$

where k is (numerically) a constant for the given conditions. It is apparent that Eq. (1) is an equation of the second degree, since the left side is the product of two variable quantities. When the pressure is plotted as a function of the volume, an equilateral hyperbola, as shown in Fig. 1, is obtained.

The actual pressure P may be thought of as consisting of the atmospheric or barometric pressure B plus an added pressure p , the algebraic sign of the added pressure depending upon whether the actual pressure is above or below atmospheric pressure. Eq. (1) may therefore be written

$$(B + p)V = k \tag{2}$$

or

$$B + p = k \times \frac{1}{V} \quad (2a)$$

By placing $1/V = x$, Eq. (2a) becomes

$$B + p = kx \quad (3)$$

or

$$p = kx - B \quad (4)$$

Since B is numerically constant (for any given case), it will be seen that Eq. (4), being of the first degree, is the equation of a straight line. If, then, not the actual pressure P but merely the added pressure p be plotted as ordinates and the reciprocal of volume, $1/V$ or x , be plotted as abscissas, the resultant curve should be a straight line (Fig. 2). If the curve is produced downward until it intersects the pressure axis, i.e., when x or $1/V$ equals zero, the intercept on the p -axis gives immediately the negative of the barometric pressure at the time of the experiment. This is obvious from Eq. (4) for if x is placed equal to 0, then

$$p = -B \quad (4a)$$

While this portion of the present experiment is designed ostensibly to furnish a check upon the approximate validity of Boyle's law, it also furnishes a splendid example of a study of both graphical and analytical representation and interpretation of experimental data. It also offers an excellent illustration of the processes used in logical scientific reasoning. When this experiment is performed with this point of view in mind, and when the differences in the apparatus, procedure and precision are considered, it will be seen that the present experiment is far from a mere repetition of one of the commonest experiments of elementary-school physics.

Charles' Law: When the temperature of a confined gas is changed, the gas will change in volume if the pressure upon it is kept constant, or it will exert different pressures if the volume is kept constant. The present experiment is restricted to a study of the variation in pressure of dry air when its temperature is changed and its volume is kept constant. Pioneer workers in this field were the Frenchmen Jacques Charles and L. J. Gay-Lussac. The law of the expansivity of gases was independently discovered by them and is variously known by each of their names. In this experiment the more common usage is followed by referring to it as *Charles' law*. These workers- and independently, John Dalton-found that *the pressure of a gas kept at constant volume changes linearly as the temperature of the gas is varied*. If the pressure is plotted against temperature, a curve similar to that shown in Fig. 3 is obtained. The equation of the straight line may be written

$$P_t = P_o(1 + \beta_v t) \quad (5)$$

where P_t represents the pressure at the temperature t and P_o is the pressure at some standard initial temperature, usually taken at 0°C . The quantity represented by, β_v is called the

temperature coefficient of pressure variation at constant volume. It is defined by the equation

$$\beta_v = \frac{P_t - P_o}{P_o t} \quad (6)$$

or, in words, *the temperature coefficient of pressure variation of a gas at constant volume is the ratio of the fractional change in pressure per unit temperature change, the initial*

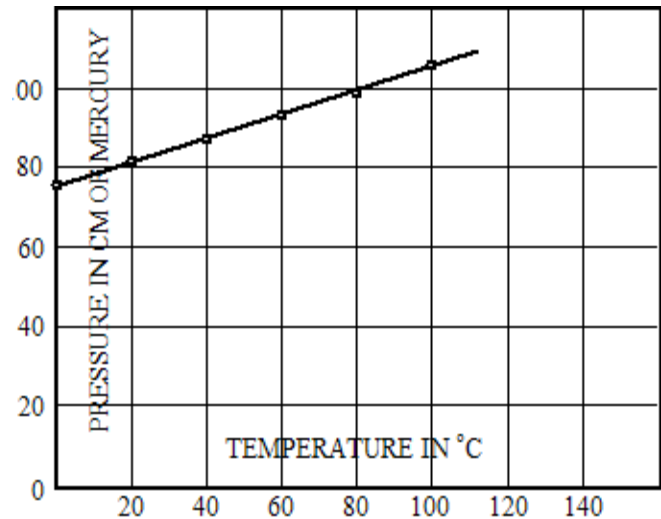


Fig. 3. Pressure against temperature, in degrees centigrade, for dry air at constant volume.

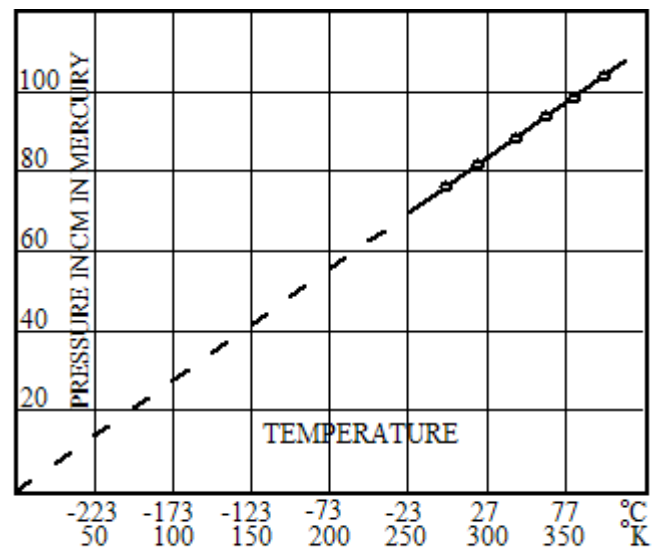


Fig. 4. Pressure against absolute temperature, in degrees Kelvin, for dry air at constant volume.

pressure being measured at a temperature of zero degrees centigrade. The slope of the pressure-temperature curve divided by P_o (the pressure when $t = 0^\circ\text{C}$) offers a convenient method for determining the coefficient of pressure variation.

It is a fact of extraordinary interest that the experimental value of, β_v for most common gases turns out to be

approximately 1/273 per degree centigrade. This means that for every degree centigrade change in temperature above or below zero degrees centigrade the pressure changes by 1/273 of the pressure which the gas exerts at zero degrees centigrade (the volume being kept constant). Hence if the temperature were lowered by 273°C below 0°C, the change of pressure would be 273 x 1/273 of P_0 or the change of pressure would equal the initial pressure at 0°C and the final pressure would be zero! This irreducible minimum of temperature is called absolute zero, i.e., the temperature of an ideal gas at which molecular activity ceases and the pressure consequently is zero. Its value is roughly checked in this experiment by extrapolating (projecting beyond the measured values) the observed pressure-temperature curve until it intersects the axis of zero pressure, as in Fig. 4. This should occur at a place where $t = -273^\circ\text{C} = 0^\circ\text{K}$ (degrees Kelvin are the units of temperature on the absolute scale of temperatures).

A careful distinction should be drawn between a linear relation and a direct proportion in the present and many similar cases. The pressure here varies linearly with the temperature in degrees centigrade, as indicated by Eq. (5) and Fig. 3. It is also true that the pressure is directly proportional to the temperature in degrees Kelvin (absolute), but the pressure is not directly proportional to the temperature expressed on any other temperature scale. This may be more clearly seen by substituting the value 1/273 for, β_v in Eq. (5) and obtaining

$$P_t = P_0 \left(1 + \frac{t}{273} \right) = P_0 \left(\frac{273 + t}{273} \right) = \frac{P_0}{273} T = CT \quad (7)$$

where T is the temperature in degrees Kelvin and C is (numerically) a constant for any given case. From Eq. (7) and Fig. 4 it is apparent that the pressure is directly proportional to the temperature only if the latter is measured on the absolute scale.

APPARATUS: The principal piece of apparatus, Fig. 5, is designed so that it may be used to study independently either Boyle's law or Charles' law. When Boyle's law is being studied, the metal-bulb reservoir shown at the left is tightly sealed off by closing a needle valve provided for that purpose and hence this portion of the apparatus may thereafter be ignored. The Boyle's law apparatus proper consists of two vertical glass tubes, one open at the top and the other closed by a stopcock, held at the lower end by stuffing boxes in an iron reservoir. The reservoir is mounted on a tripod base and is provided with a screw-operated diaphragm for varying the height of the mercury in the tubes and so changing the pressure and volume of the gas confined in the closed tube. The large, milled-head screw has a small pitch and it presses against the corrugated steel diaphragm which forms one side of the mercury reservoir. Readings of the mercury levels to measure the corresponding pressures and volumes are taken from a metric scale mounted vertically between the tubes. A sliding glass cursor provided with a horizontally etched hairline makes it conveniently possible to read the mercury levels with satisfactory precision. The air admitted to the closed tube should be carefully freed from moisture by a method

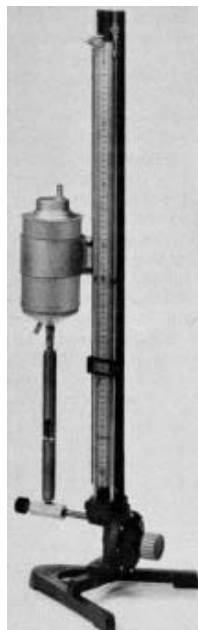


Fig. 5. Boyle's Law and Charles' Law Apparatus; an "air thermometer."

described later. The apparatus may be leveled by having the tripod adjusted on the apparatus so that the leg having the leveling screw is in the plane of the glass tubes. A slight rotation of the screw will then suffice to level the apparatus.

The Charles' law portion of the apparatus consists essentially of a metal bulb to contain the gas (air) under investigation, connected by a short section of glass capillary tubing to the mercury reservoir and manometer previously described. The volume of the gas is kept constant by adjusting the mercury level with the screw until the level is always brought to a fixed line etched on the glass tubing beneath the gas bulb. A copper jacket surrounds the bulb proper; it is provided with tubulures so that heating water may be added or removed as desired to control the temperature of the confined air. The water may be brought to and maintained at any desired temperature by an electric immersion heater, or hot or cold water

may be introduced from outside.

To facilitate reading the pressure a horizontal line has been placed on the meter stick at the side of the open tube, the line being at the same height as the etched line on the tubing of the gas bulb. When, therefore, the mercury level on the closed tube is adjusted to this etched line, the actual pressure on the gas is merely the barometric pressure plus the difference between the height of the mercury at the top of the open tube and the height of the index line.

Since Boyle's and Charles' laws do not hold for vapors it is essential that the air introduced into the gas bulb be perfectly dry.

As auxiliary apparatus there are required a mercurial barometer (Fig. 6), a 100°C thermometer, a steam generator and a Bunsen burner or an electric heater, two metal vessels for water and ice, a pinch clamp and suitable rubber tubing.

PROCEDURE:

I. Boyle's Law:

Experimental: Close tightly the needle valve which seals off the Charles' law gas bulb from the Boyle's law apparatus. Place the apparatus in good light where the scale may easily be read. Before beginning the experiment the instructor or student should be sure that the air in the closed tube is perfectly free from moisture. Introduction of dry air into the tube is effected by connecting a Dessigel S drying tube to the stopcock tube and running the mercury up and down in the tube, pumping dry air in and out and thereby removing water vapor. The stopcock tube is finally tightly closed at a place where the volume of the entrapped air is about one half the total volume of the closed tube when the levels of the mercury in both tubes are the same.

Test for leaks by turning the milled head until the mercury is near the top of the open tube and observing it for a few minutes to see that the level remains constant. Check this

also by having the mercury in the open tube near the bottom of the tube. To be sure that no air bubbles are present, turn the adjusting wheel back and forth several times to move the mercury in the open tube from the top to the bottom, meanwhile watching both tubes for bubbles. While this is being done the barometer may be read, as described below. *Never allow the level of the mercury in the tubes to come below the lower end of the meter stick, as to do so will often allow air from the reservoir to enter the closed tube and thus to vitiate the results of the experiment. During the experiment, never adjust or open the stopcock on the closed tube, as to do so will change the mass of air, admit moist air and make necessary a complete drying of a new mass of air.* As the volume of the closed tube is not calibrated directly in cubic centimeters, the volume of the gas will be measured here in terms of the length of the tube above the mercury, since the volume is proportional to the length for a uniform bore. Since it is impossible to seal the glass stopcock at the end of the tube and still have a uniform bore right up to the barrel of the stopcock, an etched line on the tube is placed at such a point that the volume in the capillary between that line and the stopcock barrel represents exactly the volume of 1cm of uniform capillary bore. Hence the corrected scale reading for the top of the enclosed air column is obtained by adding 1cm to the reading of the scale just opposite the etched line on the tube below the stopcock. This corrected value will be designated R_i .

When the apparatus is properly adjusted, take a series of ten or twelve readings of corresponding pressures and volumes, choosing the values so that the open-tube readings vary by 70mm intervals over the entire scale. Take one reading when the mercury levels are the same on the open and closed tubes. Tabulate the following: (a) R_o , the reading of the open-tube mercury level; (b) R_c , the reading of the closed-tube mercury level; (c) p , the added pressure, i.e., $R_o - R_c$; (d) P , the actual pressure, or $B + p$; (e) V , the volume or $R_i - R_c$; (f) $1/V$; (g) PV ; (h) percentage variation of PV from the average value of all PV 's. Note that when the closed-tube readings exceed those on the open tube the confined gas is below atmospheric pressure and the values of p become negative.

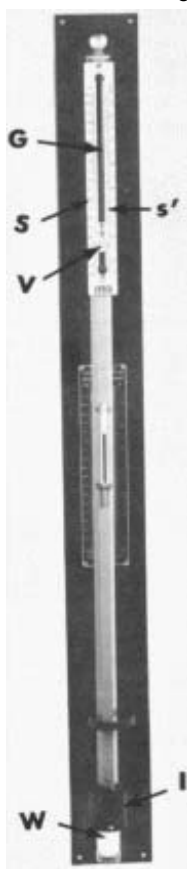


Fig. 6. Mercurial Barometer, for accurately determining the atmospheric pressure. The glass tube G, closed at its upper end, projects into the mercury cistern W. The metric and British scales S and S' have their zeros at the lower end of the ivory tip I. In reading the barometer, adjust the mercury level by turning the well upward with great care until the tip just touches the mercury surface. Move the vernier V up until the top of the mercury column appears below its lower edge. Tap the barometer lightly to permit the mercury to form a free meniscus. Then move the vernier downward until the sighting edges are in line with the uppermost point of the meniscus. Read the scale in millimeters and determine tenths with the aid of the vernier.

Interpretation of Data: Calculate the various PV products and take their average. Determine the percentage variation between the individual values of PV and their mean. What is the physical significance of the constancy of the various values of PV ?

Curves: Plot the following curves: (1) P vs. V (begin both axes at zero); (2) "added" pressure p vs. reciprocal of volume $1/V$. Choose the axis of p near the center of the page and be sure that $-p$ extends as far as 770mm below the axis. In laying off the scale for $1/V$, begin with $1/V = 0$ at the origin. Carefully interpret in the report the significance of these curves. From curve (2) determine the barometric pressure by extrapolating the observed portion of the curve (use a dotted line for extrapolated portion) back to the intercept where $1/V = 0$. Compare this pressure-intercept value of B with that observed by the barometer.

II. Charles' Law:

Experimental: A series of readings should be taken of the pressure of the air in the closed bulb when kept at constant volume and adjusted to various measurable temperatures ranging from 0°C to 100°C . The end temperatures will be the standard values for the freezing and boiling temperatures of water, while the intermediate values are to be read by a mercury thermometer. The pressures are obtained from the barometric height and the open-tube manometer.

Fill the water jacket with a mixture of chipped ice and water. After equilibrium is attained, adjust the pressure until the mercury is brought to the line etched on the glass in the open portion of the metal tubing. Measure the actual pressure P on the gas as given by where M is the height of the mercury in the open tube and l is the height of the index line.

Heat the ice water to about 20°C by means of the electric heater (or run it off and introduce other water at room temperature), adjust the volume to the fixed value as before and again read the pressure and temperature. Repeat this process by approximately 20°C intervals until the water is near the boiling temperature. A final convenient value to observe is the one in which steam is passed to the upper tubulure from a steam generator. Arrange a rubber tube from the lower tubulure to a suitable vessel to catch the condensed water vapor.

WARNING! As the steam enters the jacket, the mercury in the gas tube will descend and may go below the lower end of the meter stick and admit air to the bulb. This should be prevented by raising the pressure to keep the level of the mercury on the gas-bulb tube at the index Line. Throughout the entire experiment one observer should continually observe the pressure and keep adjusting the screw to maintain the mercury levels at the desired values. When the hot water is removed from the vessel or when the steam is discontinued, the pressure will greatly decrease and the mercury might run up into the closed bulb if the adjusting screw were not manipulated to lower the level of the mercury in the closed tube.

The temperature of the steam is best obtained from a table of boiling points against pressure.

Interpretation of Data: Plot a curve to show the variation of

the pressure with the temperature in degrees centigrade. Explain clearly the significance of the shape of this curve. Determine the slope of the curve, choosing points near its ends, and divide the slope by P_0 . This should give the value of, β_v ; determine the percentage difference between this value and the standard value, 0.003663 per degree centigrade.

Plot another curve from the observed data showing the variation of pressure with temperature, but starting the pressure scale with zero and the temperature scale with -273°C (0°K). Include on the temperature scale the values in both degrees Kelvin and degrees centigrade. Extrapolate by a dotted line the observed data to the axis of zero pressure. Compare this temperature intercept with the standard value for absolute zero. What is the ratio of the slope of the curve and the pressure at 0°C ? Explain in the report the significance of the curve.

QUESTIONS: 1. Show by dimensional reasoning that the constant k in the equation $PV = k$ is not a mere numerical constant, i.e., one having no unit, but that it has the dimensions of work. On what does the value of k depend?

2. A certain automobile tire is labeled, "Inflate to 35lb. or 2.5kg." What does this mean? Is the statement clear? Is 35lb. equal to 2.5kg?

3. The gas bulb of the Charles' law apparatus is made of cast iron. What happens to its volume when the temperature is changed from 0°C to 100°C ? What effect does this have upon the "constant volume" assumption? Is the error serious? Why?

4. In the Charles' law apparatus as used, a portion of the air bulb is connected to the mercury reservoir by a glass capillary tube, the level of the mercury always being brought to a fixed point on this tube. Hence some of the air above this line but below the metal bulb is not subject to the same temperature as the air inside the bulb. Will this introduce a serious error into the results? Why?

5. The level of the mercury in the open arm of a Charles' law apparatus stands 5cm below the index when the volume bulb is surrounded by ice water, and 20cm above the index when the bulb is surrounded by steam at normal barometric pressure. Calculate the temperature coefficient of pressure variation at constant volume from these data.

6. The pressure of a gas is measured as 100cm of mercury at 50°C and 114.3cm of mercury at 100°C , volume constant. What value of absolute zero is obtained from these data?