

CHARLES' LAW

OBJECT: To study the expansion of gases, to check Charles' law and to measure the temperature coefficient of pressure increase of dry air at Constant volume.

METHOD: 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 determined approximately.

THEORY: 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 frequent 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. 1 is obtained. The equation of the straight line may be written

$$P_t = P_0(1 + \beta_v t) \quad (1)$$

where P_t represents the pressure at the temperature t and P_0 is the pressure at some standard initial temperature, usually taken at 0°C . The quantity represented by, β_v is called the coefficient of pressure variation at constant volume. It is defined by the equation

$$\beta_v = \frac{P_t - P_0}{P_0 t} \quad (2)$$

or, in words, *the coefficient of pressure variation of a gas at Constant volume is the fractional change in pressure per unit temperature change, the initial pressure being measured at a temperature of zero degrees centigrade*. The slope of the pressure-temperature curve divided by P_0 (the pressure when $t = 0^\circ\text{C}$) offers a convenient method for determining the coefficient of pressure increase.

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 centigrade degree. This means that for every centigrade degree change in temperature above or

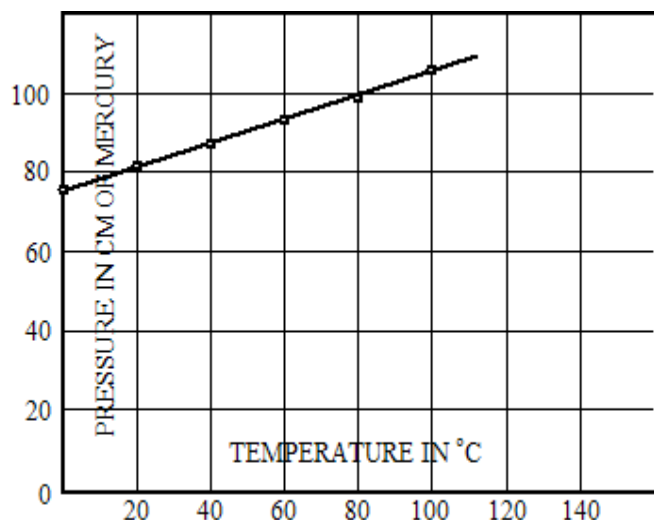


Fig. 1. Pressure against temperature, in degrees centigrade, for dry air at constant volume.

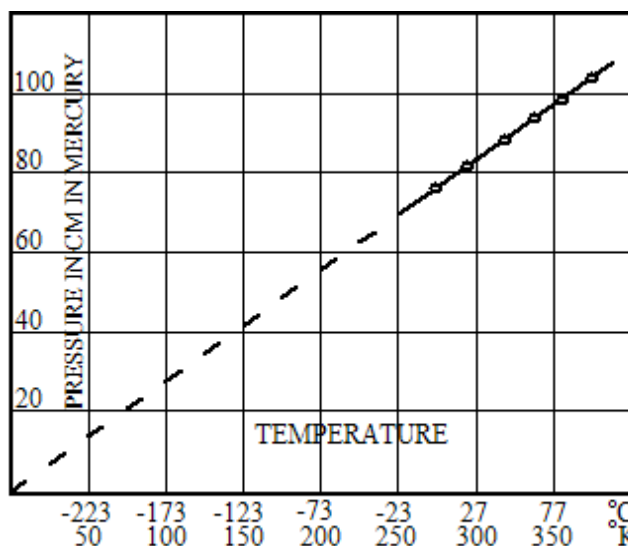


Fig. 2. Pressure against absolute temperature, in degrees Kelvin, for dry air at constant volume.

for every centigrade degree 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 $273 \times 1/273$ 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. 2. This should occur at a place where $t = -273^\circ\text{C} = 0^\circ\text{K}$ (Kelvin degrees 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

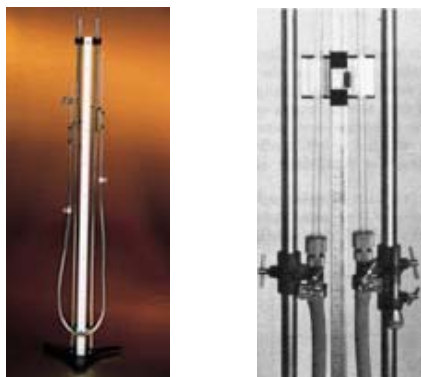


Fig. 3. Charles's Law Apparatus, or Constant-Volume Air Thermometer. Insert shows "close-up" of reading device.

similar cases. The pressure here *varies linearly* with the temperature *in degrees centigrade*, as indicated by Eq. (1) and Fig. 1. 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. (1) and obtaining

$$P_t + P_0 \left(1 + \frac{t}{273} \right) = P_0 \left(\frac{273 + t}{273} \right) = \frac{P_0}{273} T + CT \quad (3)$$

where T = temperature in degrees Kelvin and C is a constant for any given case. From Eq. (3) and Fig. 2 it is apparent that the pressure is directly proportional to the temperature only if the latter is measured on the absolute scale.

APPARATUS: The Charles' law apparatus, or constant-volume air thermometer, is shown in Fig. 3. It consists essentially of a glass bulb, containing the air under investigation, connected by a flexible rubber tube to an open-arm mercury manometer. The bulb and manometer are assembled on a heavy supporting frame, held on a tripod base which is provided with leveling screws. Between the

vertical support rods is mounted a square metal meter scale to provide accurate determination of the positions of the mercury columns in the communicating glass tubes. Either the closed-bulb arm or the open, funnel-tube arm of the manometer may be raised or lowered on the support rods in order to vary the pressure on the air in the bulb. This pressure is read in terms of the difference in the mercury levels in the two arms, the readings of the levels being obtained by means of a sliding mirror index moving along the graduated square tube and upon which a fine horizontal line is etched. This permits setting the index on the mercury columns without parallax. After the setting has been made, the reading is taken from a vernier engraved upon the mirror sleeve. The reading device is held in any desired position on the graduated tube by means of spring friction. The clamp which holds the open tube is provided with a micrometer adjusting screw by means of which small variations of the pressure may conveniently be made with precision. To vary the temperature of the gas under examination, the gas bulb may be immersed in an ice bath, then in water at various temperatures and finally in a steam bath. The volume is kept Constant by adjusting the pressure until the mercury level on the closed bulb is brought each time to a line etched on the glass just above the stopcock. The three-way stopcock between the bulb and the manometer permits filling the bulb with dry air or any other gas desired. The glass gas bulb is connected to the manometer through a heavy-walled capillary tube of negligible volume. The glass tubes are sealed with a special pressure-tight wax into the upper part of steel couplings, the lower portion of the couplings being connected to the upper portion by means of a hexagonal nut which tightly presses upon a rubber gasket. The rubber hose is sealed upon the lower portion of the coupling by rubber cement. These precautions are essential to prevent leaks.

Great care must be observed in adjusting the cooling and heating baths around the gas bulb so as not to break the necessarily fragile tube connecting the bulb and the manometer. Be sure that the stopcock is greased and held on by rubber bands. When the open tube is turned in toward the mirror, pains must be taken not to hit it against the top of the support.

As auxiliary apparatus there are required a drying tube, a thermometer of range 0° to 100°C , a Bunsen burner, cracked ice, a barometer, a steam generator and an electric heater.

PROCEDURE:

Experimental: Before beginning the experiment the gas bulb must be filled with the proper mass of completely dry air. This will, in general, have been done previously by the instructor. Hence the stopcock should not be tampered with. If for any reason it becomes necessary again to fill the bulb it may be done by connecting the proper outlet of the three-way stopcock through a Dessigel S drying tube to an air pump and pumping the dried air into and out of the bulb a large number of times.

A series of readings will 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 .

Arrange the ice bath around the gas bulb, lowering the arm containing the bulb until the latter is conveniently within the ice pail, meanwhile suitably lowering also the open tube of the manometer. Pack the gas bulb with a mixture of crushed ice and water, taking care to lower the open arm of the manometer to prevent the reduced pressure of the chilled air from allowing the mercury to run into the bulb. After temperature equilibrium is attained, adjust the pressure until the mercury is brought in the capillary to the index line etched upon the closed tube. Read the levels of the mercury in both arms and, by subtraction, obtain the pressure which must be added to the atmospheric pressure to give the actual pressure of the air. The atmospheric pressure is obtained by reading the barometer (Fig. 4). (The difference in the mercury levels must be *subtracted from* the atmospheric pressure if the level of the mercury in the open tube is *below* that of the index on the closed tube.)

Remove the ice water and replace it by water at room temperature. Adjust the volume to the fixed value, as before, read the mercury levels, and determine the actual pressure. Note the temperature of the water from the thermometer. See that the water is well stirred and that equilibrium conditions are attained before final readings of pressures and temperature are taken.

Repeat these observations by heating the water by approximately 20°C intervals until it is near the boiling temperature. The water may be heated by an electric immersion heater, or an ordinary steam generator may be used to heat water which can be transferred to the bath surrounding the bulb. The temperature of the steam is best obtained from a table of boiling points against pressure.

WARNING! When the temperature of the gas is suddenly changed, as for example when the steam is admitted or removed, the pressure will undergo a violent change. This may allow mercury to be forced completely out of the closed tube or to enter the gas bulb unless proper precautions are observed suitably to vary the level of the mercury in the open tube. Throughout the experiment, and especially when the gas bulb is to be subjected to drastic temperature changes, one observer should continually check the pressure and keep adjusting the level of the open tube to maintain the volume in the closed tube at or near the desired value.

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 centigrade degree.

Plot a curve from the observed data showing the variation of pressure with absolute temperature. Start the pressure scale with zero and the temperature scale with -273°C or 0°K. Include the values of the temperature in both degrees centigrade and degrees Kelvin on the temperature scale. 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.

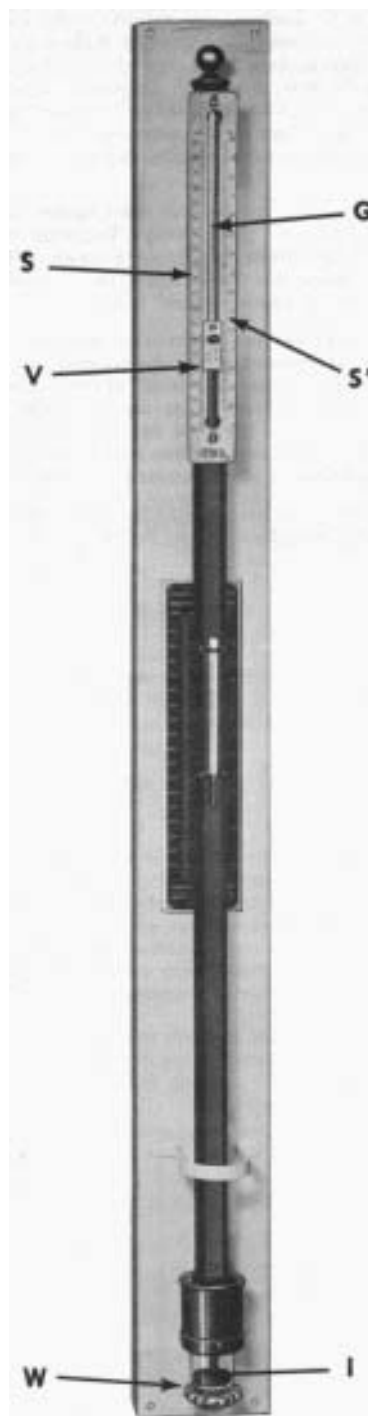


Fig. 4. Mercurial Barometer, for accurately determining the atmospheric pressure. The glass tube G, closed at its upper end, projects into the mercury cistern W. The metric and British scales S and S' have their zeros at the lower end of the ivory tip I. In reading the barometer, adjust the mercury level 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.

QUESTIONS: 1. The gas bulb of the Charles' law apparatus is made of "Pyrex" glass. 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?

2. In the Charles' law apparatus as used, a portion of the air bulb is connected to the mercury manometer 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 outside the gas bulb is not subject to the same temperature as the air inside the bulb. Will this introduce a serious error into the results? Why?

3. The level of the mercury in the open arm of a Charles' law apparatus stands 5.00cm below the index when the volume bulb is surrounded by ice water, and 20.0cm above the index when the bulb is surrounded by steam at normal barometric pressure. Calculate the coefficient of pressure increase at constant volume from these data.

4. The pressure of a gas is measured as 100.0cm 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?

5. An automobile tire gage registers a pressure of 35 lb./sq. in. at the start of a trip after 10 miles of driving the same tire gage registers 37lb./sq. in. on the same tire although no air has been added and the barometric pressure is unchanged. Explain what pressure the tire gage reads and account for the difference in readings by some physical law. Assume the tire gage reads perfectly.

6. The pressure of the gas in a gas thermometer is 76.5 cm of mercury at 27.0°C . By how much will the pressure increase when the temperature rises 1.0°C ?

7. The temperature of air supplied to a furnace is increased from 27 to 77°C . If the mass of oxygen in each cubic foot of air supplied is to remain the same, by what percent must the pressure of the air be changed?