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individual scientists to insist upon the correct use of abbreviations and symbols, and it is very understandable that the publishers will consider this request of the publishing scientist.

In order to spare a lot of explaining and argumentation the author suggests that the Minnesota Academy of Science, as an organized body of scientists, shall make recommendations to publishers to use abbreviations of the metric system and their multiples and fractions as adopted by the International Bureau of Weights and Measures, excepted and ratified by most of the nations, including the United States of America (in 1868).

Science which claims to be international shall set an example by using its units with all implications uniformly. It would be a noble contribution of the Minnesota Academy of Science to science as well as to the world of tomorrow, if the Academy would initiate and sponsor the promotion of unification of symbols and abbreviations.

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TWO PHYSICAL METHODS FOR THE QUANTITATIVE DETERMINATION OF ONE COMPONENT OF A MIXTURE OF GASES*

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It is often desirable to make a quick and fairly accurate determination of the relative percentages of the constitutents of a mixture of gases. The most common method used for making a quantitative analysis of a mixture of gases is that of measuring the volume of the gas before and after passing it through each of a series of absorption chambers, one constituent of the mixture being removed in each chamber by absorption or by a chemical reaction. This method may not be satisfactory for the complete analysis of a mixture of gases if two or more of the constituents are chemically inert, such as mixtures containing both nitrogen and helium. The two methods to be described can be used for the quantitative analysis of two of the constituents of a mixture if the relative percentages

of the other constituents are known or they may be used to indicate that a change in some one of the constituents has taken place. We have used both methods for the quantitative analysis of gases used as anesthetic or as therapeutic agents.[1-3]

The velocity of sound in a gas and the effusion time of a gas depend on several factors, the most important of which is the density of the gas. Neither of these two methods can be used for the quantitative analysis of mixtures of gases having nearly the same density. Both methods have been used in the past by others in studies of various properties of gases and mixtures of gases; the applications described here are specific examples of the use of these two methods.

VELOCITY OF SOUND

The apparatus we have used for the measurement of the velocity of sound in a gas is shown in figure 1. The gas space in the apparatus must be thoroughly flushed out with the gas to be analyzed.
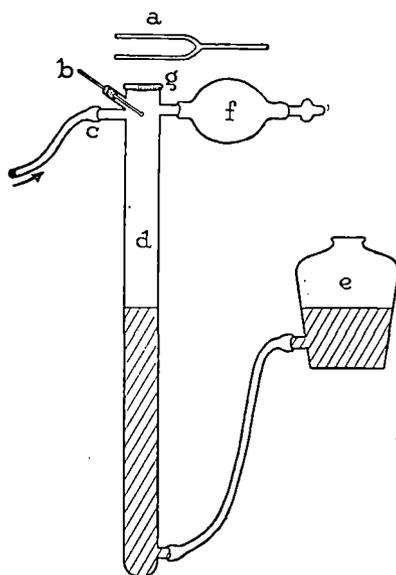

Fig. 1. Apparatus for determining the velocity of sound in a gas. a, Tuning fork; b, thermometer; c, tube through which gas is admitted; d, glass tube; e, water reservoir; f, rubber bag; g, rubber diaphragm over upper end of glass tube.

The tuning fork is struck and, while it is humming, the column of water is lowered gradually until a point of resonance is found. The column is then lowered again to a second point of resonance.

These points are marked on the tube with a wax pencil and the distance between them is measured. This distance, which is half a wavelength, multiplied by two and by the frequency of the tuning fork gives the measured velocity of sound.

When water is used as the liquid in the tube the gas will be saturated with water vapor and the density of the gas and the velocity of sound will be different from what they would be in a mixture of dry gases. Ethylene glycol has also been used instead of water. It has a negligible vapor pressure but absorbs water vapor freely; therefore, to prevent its becoming diluted, the gases were dried by being passed through tubes containing calcium chloride before they entered the apparatus. Water is easier to use than ethylene glycol and does not introduce an error if the presence of water vapor is taken into account when the velocity of sound is calculated.

The velocity of sound in a gas can be calculated from the formula

$$V = \sqrt{\frac{\gamma\, P}{d}}$$

where $V =$ velocity in centimeters per second, $\gamma =$ the ratio of the specific heat at constant pressure to that at constant volume, $P =$ pressure in dynes per square centimeter and $d =$ density of the gas in grams per cubic centimeter.

The value of γ is different for different gases and varies with temperature; the variation of value for the different gases we have used is rather small compared to the variation of their density; the variation with the temperature is negligible. Since changes of pressure produce a proportionate change of density, the velocity does not vary with changes of pressure. Changes of temperature do produce a change of density which must be taken into account.

The calculated values for the velocity of sound in various mixtures of oxygen, helium and nitrogen have been plotted in figure 2. To analyze a mixture of these three gases it is necessary to determine the velocity of sound in the mixture, as described in preceding paragraphs, and the volume percentage of oxygen present by any standard method; the volume percentages of nitrogen and helium are then determined from the graph. Analyses of mixtures of these three gases by this method can easily be made with an accuracy of ± 2 per cent or less.

Faulconer, Clarke and Osterberg[4] used a modification of this apparatus as a continuous indicator of the constancy of, or to analyze mixtures of, anesthetic gases. They used an electric oscillator instead of a tuning fork. A microphone coupled to an amplifier system caused a signal light to be turned on when a point of resonance was reached.
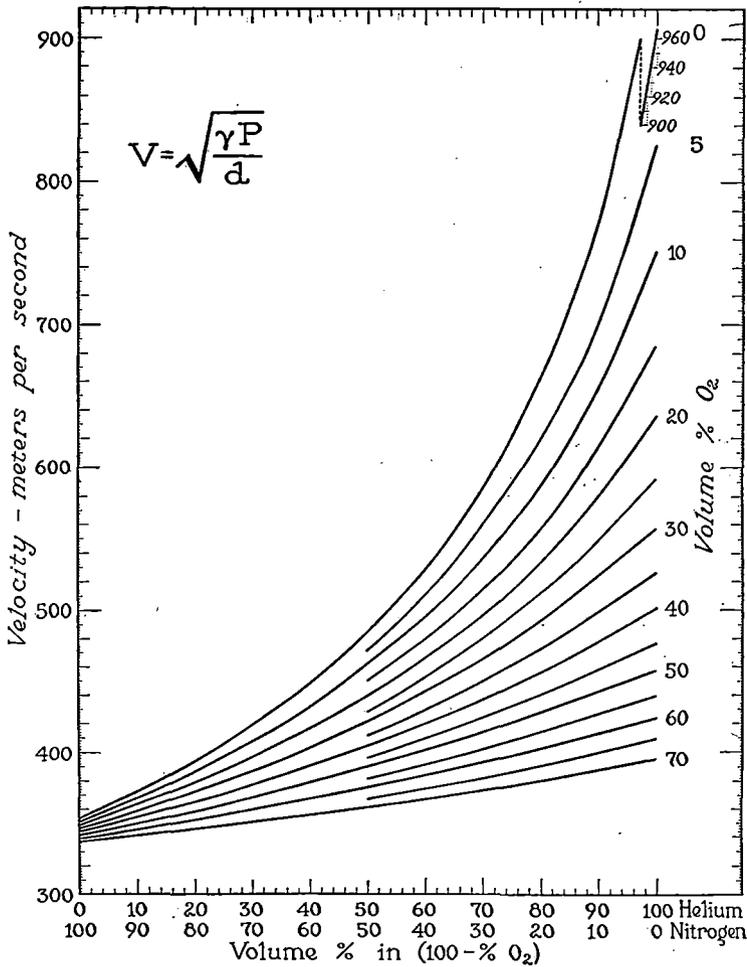
Fig. 2. The velocities of sound at 24° C. for volumetric percentage combinations of oxygen, helium and nitrogen saturated with water vapor. Percentages on the chart for nitrogen and helium are those in the quantity remaining after deducting oxygen.

EFFUSION TIME

In 1833 Thomas Graham [5] stated that the effusion time of gases through very small orifices is proportional to the square root of their densities. This statement is generally referred to as Graham's law. While many attempts have been made to derive a theoretical expression for the effusion time, it is very difficult to construct a piece of apparatus that fulfills all the theoretical requirements. Theoretically the diameter of the hole must be small compared to

the mean free path of the molecules and the length of the hole must be small compared to the diameter. Practically, holes of the order of a few thousandths of an inch in plates of similar thickness are fairly satisfactory. The effective size of the hole may be very different from the apparent size and will depend on how sharp the edges are and the shape of the hole. The presence of a vapor in the gas is likely to cause inconsistent results, due to condensation of the vapor around the orifice, which may change its effective size. The effusion of gases through orifices of practical size is also affected by their viscosity.

The effusion time depends on the difference of pressure on the two sides of the orifice; the rate of effusion increases as the difference of pressure is increased until the velocity of the gas through the orifice is equal to the velocity of sound in the gas. At velocities equal to the velocity of sound no pressure can be propagated backward. Lamb [6] showed that the velocity of sound should be reached when the low pressure is 0.527 that of the higher pressure. Since the velocity of sound in a gas depends on the value of γ (ratio of specific heats) for the gas, the effusion time will be affected by variations of γ as well as by varitions of density but ordinarily the variations of γ are small compared to the variations of density. From the practical standpoint it is generally desirable to have a pressure differential of more than 2:1 so that the effusion time is independent of the pressure and hence there is no necessity of measuring the pressure.

In figure 3 is a diagram of the apparatus we have used. The orifice was a hole 0.005 inch (0.127 mm.) in diameter in an Everdur metal disk 0.005 inch (0.127 mm.) thick.* By connecting the mercury reservoir to a vacuum pump the mercury can be made to flow from the gas bulb to a level below E if the stopcock is open to admit air or a sample of the gas to be analyzed. The gas bulb and orifice chamber should be thoroughly flushed out with the gas to be analyzed before the effusion time is determined and the gas should remain in the bulb a few minutes to allow its temperature to come into equilibrium with that of the water bath. The gas bulb should be filled with the gas to a position below E when the mercury reservoir is open to atmospheric pressure. The orifice chamber is connected to a vacuum pump which will maintain a pressure of less than 0.5 atmosphere above the orifice. The stopcock, which will have been in a closed position after the gas was introduced into the gas bulb, is then turned to connect the gas bulb to the orifice chamber. The effusion time is the time it takes the mercury to rise from

* The metal disk was made of Everdur, an extremely hard and rigid metal. The hole was bored very carefully and its diameter was determined under a microscope with a micrometer. The walls of the orifice were very smooth and the edges were clean and rounded. Through the courtesy of Mr. James I. Banash we obtained the effusion disk from the Union Carbide and Carbon Corporation.
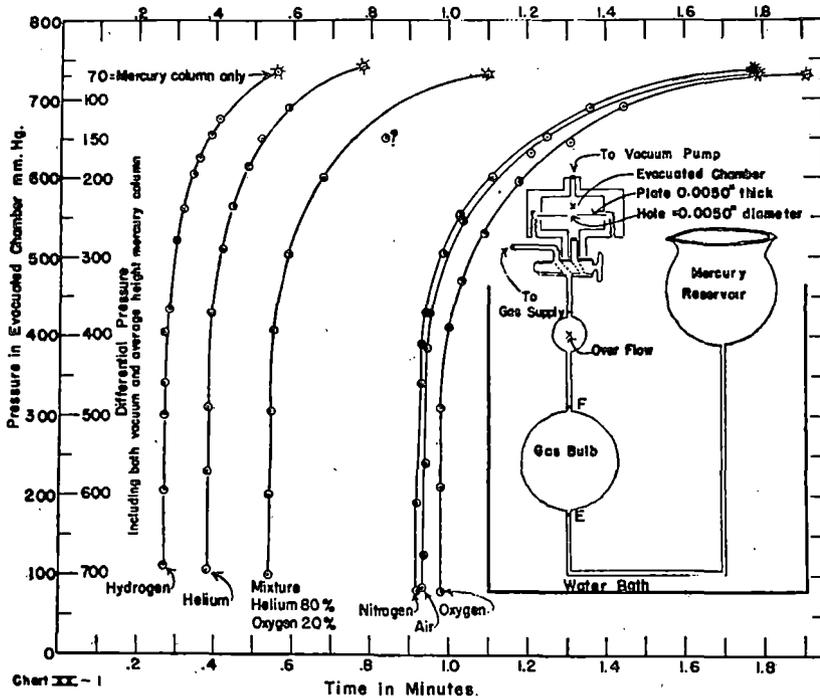
Fig. 3. Apparatus for determining the effusion time of a gas through an orifice and graphs of the effusion time for various gases through the orifice for different pressures.

E to F. The stopcock is closed while mercury is flowing into the overflow bulb and before it gets to the stopcock.

The effusion times measured for several gases are plotted in figure 3. In obtaining the data from which these graphs were drawn, the pressure above the orifice was not maintained at less than 0.5 atmosphere, as stated previously, but was adjusted to the desired value. It is seen that the effusion time of each gas decreases as the differential pressure increases until a value of about 400 mm. of mercury is reached but a further increase of differential pressure does not change the effusion time. In figure 4 the same data are plotted to show that the effusion time for a constant differential pressure is proportional to the square root of the molecular weight.

The data shown in figures 3 and 4, as well as data on many other gases and mixtures of gases, verify the statement that the effusion time is a function of the differential pressure until this pressure reaches a value of about 2:1. The data shown in figure 4 verify Graham's law that effusion time is proportional to the square root of the molecular weight. The effusion time for some mixtures of anesthetic gases does not fit on the curves of figure 4, probably because these
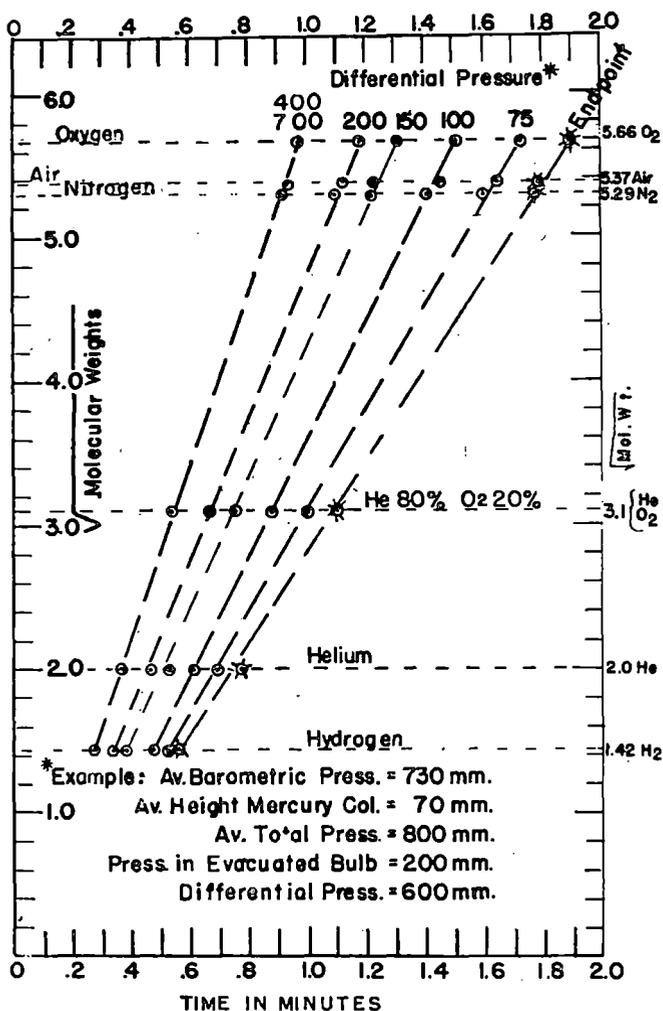
Fig. 4. Data on effusion time from figure 3 plotted to show that for a given differential pressure across the orifice the effusion time is proportional to the square root of the molecular weight of the gas.

mixtures contain vapors and hence do not behave like true gases and also because they may have different viscosities and ratios of specific heat. The viscosities and ratios of specific heat of the gases shown in figure 4 are not all the same but apparently the variations are negligible as far as the effect on effusion time is concerned.

Although the value of the effusion time for a particular gas may

not fall on the graphs of figure 4, a mixture containing this gas can still be analyzed by the effusion method. Data can be obtained from a few known mixtures and a graph drawn showing the relationship between effusion time and composition of the mixture. This has been done for certain mixtures of anesthetic gases but work with these mixtures was interrupted by the war.

Since the rate of flow of a gas through an orifice is a function of the differential pressure, it is possible to use an orifice, or a group of orifices, as a flowmeter for a gas. For this purpose a manometer measuring the difference of pressure on the two sides of the orifices is calibrated to give volume flow per unit of time; such a flowmeter must be calibrated for each gas or mixture of gases with which it is used, since effusion time varies with different gases. A somewhat similar flowmeter practically independent of density of the gas, thus allowing the same calibration to be used for many gases, can be made by using tubes or sponge rubber instead of orifices, for the flow of gases through tubes or sponge rubber is entirely different from effusion through an orifice.

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