angles associated with them. Apart from the pure geometric beauty exhibited by these "fished" single crystals, the geometric patterns could be studied for crystal growth orientation.

Figs. 2 *A*, 2 *B*, and 2 *C* show quite clear crystal structures which have been "fished" out from their growth environment very quickly. There is some disorder associated with the faces shown, but this is due to adherence of small amounts of germanium to the growing planes. When the growth is "fished" out these small amounts of germanium quickly freeze in a disordered fashion. They are not found when surfaces grow naturally without being subjected to rapid dislocation and extreme changes in temperature.

We regret that we cannot supply samples of these "fished" crystals, for our supply is limited.

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The Pirani Gauge

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The wide application of the Pirani gauge (*1*) as a heat conductivity manometer is evident from the excellent review of the literature by Dushman (*2*). Chief among the advantages and disadvantages of such a device for measuring pressures in the molecular and transmolecular regions are those given by DuMond and Pickels (*3*), von Ubisch (*4*), and others (*2*, p. 368), summarized in the following statements: (1) It is most suitable at very low pressures; (2) thin filaments insure a quick response at low pressures and a greater sensitivity at higher pressures; (3) materials available for filaments are sufficient so that pressures of many gases, corrosive and otherwise, may be measured; (4) by special design the instrument may be used to measure pressures over a wide range. The main disadvantages are (1) The shift of the "zero" point and (2) the increase of the ratio of radiation loss at pressures below 10^{-3} mm Hg, since at these low pressures the molecules of gas travel in straight lines between the wire and the walls, just as the photons of radiation do.

The range of pressures for which the Pirani gauge operates satisfactorily is from 10^{-4} mm to 10^{-1} mm of Hg (*2*, p. 367). Some experimenters, however, have extended this range to a lower limit of 10^{-5} mm (*5*) and to an upper limit of 50 mm (*6*) by modifying the design of the gauge.

The main disadvantage of the Pirani gauge, which has heretofore restricted its lower limit to 10^{-4} mm because of the so-called zero drift, has been studied by Kersten and Brinkman (*5*). Their solution to the problem is the construction of three identical gauges, two of which are exhausted, outgassed, and sealed off, and the third is connected to the vacuum system. By inserting one of the sealed-off gauges, called the reference gauge, and the measuring gauge in adjacent arms of a Wheatstone bridge, these authors obtained a balance point of the bridge which is indifferent to fluctuations of the bridge potential or to small changes in the temperature of the surroundings of the gauge. The second sealed-off gauge, called the zero gauge, is mounted in a separate branch of the circuit and heated to about the same temperature as the reference gauge. With such an arrangement the time required to attain equilibrium was very small. Since the heating of the measuring gauge was continued, it was possible to start the pressure measurements immediately after finishing the zero point control. With this arrangement and an applied heating current at the ultimate vacuum of 6.4 ma the deflection of the bridge meter was directly proportional to the gas pressure from 0 up to about 0.02 mm Hg. Beyond this region the sensitivity of the gauge-bridge combination decreased rapidly with increasing pressure.

In order to extend the use of the Pirani gauge to regions of higher pressures Rittner (*7*) applied the controversial point of the influence of wire-to-wall distance as a determining factor in the pressure measuring range. He used a convenient length of 1 mil tungsten wire and suspended it coaxially inside a piece of 2 mm capillary Pyrex, fitted with a glass side tube. The gauge was operated at constant resistance in a Wheatstone bridge by varying the applied voltage and measuring the total bridge current required to establish balance. The gauge was immersed in an ice bath. The author claims a precision of measurement of $\pm 2.5 \times 10^{-4}$ mm at low pressures, where the sensitivity was greatest, and ± 0.35 mm at 15 mm, where the gauge sensitivity was falling rapidly. This is equivalent to a precision of ± 2.5% or better over the pressure range 10 μ to 15 mm.

Von Ubisch (*8*, *9*) modified the electrical circuit of the Pirani and thereby measured pressures up to 50 mm Hg. The gauge is an extended spiral of 0.01 mm tungsten wire of approximtaely 5 cm length mounted inside a capillary. A regenerative feedback is provided through the bridge containing the hot wire. The amplitude of oscillations adjusted itself to keep the temperature of the wire approximately constant at all pressures. The range of heating current extended from 4 to 35 ma for a corresponding pressure range of 10^{-3} mm to 50 mm Hg.

The effect of wire-to-wall distance in the measurement of pressures of rarefied gases is a controversial problem (*10*). Kersten and Brinkman (*5*) quote Knudsen's theory that the use of the hot wire gauge is based upon the principle that the thermal conductivity of a gas is directly proportional to the pressure as long as the mean free path of the molecules is larger than certain distances within the measuring system. Von Ubisch (*11*) confirmed the fact that in order to insure proportionality between pressure and heat conductivity, it is sufficient that the diameter of the wire be small compared with the mean free path of the molecule. He observed a deviation of 10% from proportionality if the mean free path of the molecule was about seven times the diameter of the wire and a somewhat lower factor than seven for a ribbon.

In agreement with those who favor the influence of wire-to-wall distance is the work of Rittner (*7*) who based the success of his experiment in extending the range of pressure to 10 mm on the fact that he decreased this wire-to-wall distance to a minimum by use of a capillary. However, as is pointed out (*10*), Rittner did use a very fine wire (0.01 mm).

The effect of spirals in manometry gauges is summarized by von Ubisch (*12*). Spirals behave as if they have a surface which is smaller than the surface of the wire from which they are made. The reason is that the turns partially shield one another. However, the coefficients of emissivity and of accommodation for the spiral are increased. The heat radiation that originates from the inner parts of the spiral is partially reflected outward and adds to that from the visible parts. Because of repeated impacts the molecule would leave the spiral with more energy than it would after collision with a straight wire. But as emissivity coefficients are of the order of 0.1 and the accommodation coefficients for a single impact range from 0.3 to 1.0, and neither coefficient finally increases above unity, spirals have an increased rate of radiation relative to conduction. It may be concluded that although spirals do decrease the sensitivity of the gauge, the advantage of increased length of the filament compensates for this factor.

A universal agreement (*10*) among investigators is the importance of heating the wire to a higher temperature than is normally employed and of maintaining this required higher temperature as the pressure rises. Von Ubisch (*11*) recommends 100° C for all filaments, as being sufficiently above room temperature and giving about a maximum of sensitivity for medium lengths of filaments.

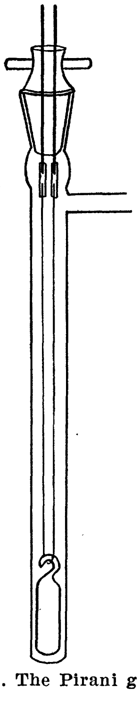

FIG. 1. The Pirani gauge.

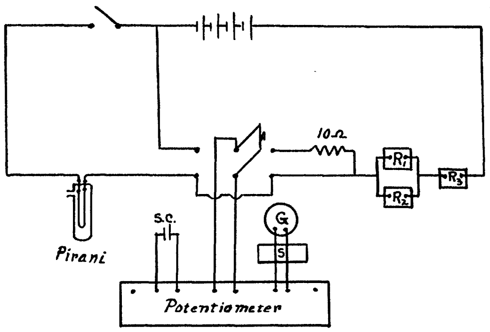

FIG. 2. Wiring diagram for circuit containing the Pirani gauge. R_1 and R_3 are 10,000 ohm decade boxes, R_2 is a 1000.0 ohm decade box. *S.C.*, standard cell for potentiometer; *G*, galvanometer, *S*, shunt.

A Pirani gauge was designed that includes a number of features that make it simple in construction, rugged, sensitive to small pressure changes, and capable of reproducing results. The gauge and wiring diagram are shown in Figs. 1 and 2. The over-all length of the gauge is 16 cm. The tube is 9 mm OD Pyrex with ground-glass fitting, sealed with a beeswax and rosin mixture. This fitting permitted a rapid replacement of the filament wire. Both platinum and tungsten filaments were used, but the latter proved far more durable, although less sensitive for the same heating current. The present filament has been heated at 40 ma for over 500 hr. Several of the platinum filaments burned out after 50 hr. However, in the case of platinum, using a 0.025 mm filament, 16 cm long, a heating current of 26 ma resulted in a sensitivity of 6.6 v/mm Hg for nitrogen, whereas the same size filament of tungsten required a heating current of 40 ma for a sensitivity of 5.1 v/mm Hg. The filament is supported by 2 tungsten leads 0.76 mm in diameter and kept taut by a 2.3-g glass weight hooked over the loop of wire. Nickel sleeves were slipped over each lead and the ends of the filament wire and fastened by crimping at several places. The gauge was immersed in a 5-liter Dewar of crushed ice and water. A high-speed stirrer maintained a constant 0° temperature during the calibrations. Other methods, such as a shielded air bath and a bath of continuously flowing tap water, proved unsatisfactory because of the sensitivity of the gauge.

A 6-v storage battery connected in series with one 10,000 ohm (R_1) and one 1000.0 ohm (R_2) decade boxes in parallel, and one 10,000 ohm (R_3) decade box in series, heated the gauge. A type K-1 potentiometer was used to determine both the heating current and the potential drop across the Pirani. This was accomplished by placing a 10 ohm standard resistance in the circuit used to measure the heating current and connecting the two circuits to the poten-

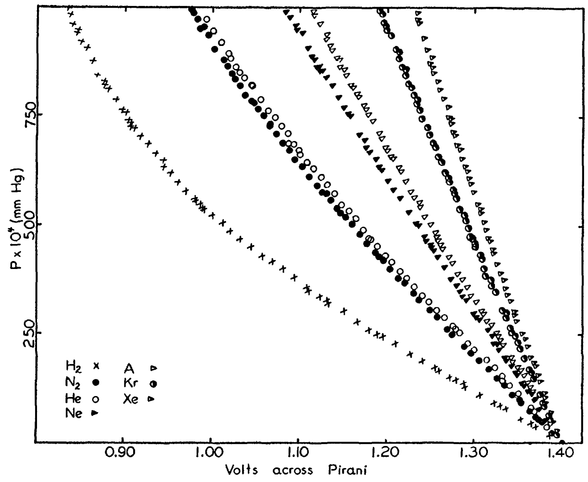

FIG. 3. Calibration curves for five rare gases, nitrogen, and hydrogen. Each curve represents four calibrations for both increase and decrease of pressure. The same gas was not used for any two successive calibrations.

tiometer by means of a double-pole double-throw switch. The sensitivity of the gauge necessitated using the shunt on 0.1. The heating current was maintained exactly at 40.000 ma by adjusting the resistances after each addition of gas. This value permitted the use of the potentiometer in the 1.6-v range. Sixty ma heated the gauge to a dull red, visible only in the dark.

The pressure in the system, except during the periods of calibration, was maintained at from 10^{-6} to 10^{-4} mm Hg. Cold traps of dry ice and acetone prevented the mercury vapor from entering the Pirani. Initially the filament was heated to redness and the system flushed with hydrogen in order to clean the surface of the tungsten. Although the treatment was not as extensive as that suggested by Norton and Marshall (*2*, p. 737), the results indicated that such a process proved essential in obtaining reproducible results. If air was accidentally introduced into the system while the Pirani was heated and the gauge was then calibrated with hydrogen, the resulting curve was quite erratic. However, this clean-up process with hydrogen re-established the previous results.

A ½-hr preheating of the filament at 0 pressure was adequate. Several readings of the voltage across the Pirani were taken during this time until a constant value was obtained. This reading then served as the zero reading. In order to determine the extent of the zero drift, the Pirani was heated at 40 ma and zero pressure and observed at ½-hr intervals for several days. From 0.05 to 0.1% drift during 7 hr was observed. If this deviation from some established zero point was corrected for at the various voltage determinations, the calibration curves were definitely reproducible.

Five rare gases, hydrogen, and nitrogen were used as calibrating gases. Xenon, krypton, and neon contained spectroscopic traces of impurities; argon was tank argon passed over hot uranium; helium was Grade A, 99.99% pure; the hydrogen was electrolytic hydrogen passed through a "Deoxo" and a liquid air trap. The nitrogen was obtained from two sources: heated sodium azide, and tank nitrogen passed through a dehydrating agent. The curves for the two sources of nitrogen were indistinguishable. Liter bulbs containing these bases were mounted on the system and connected to a main gas line by microgas burettes (*13*). By this means, small and measurable quantities of gas, sufficient to change the pressure of the system in the range of 0.0005 mm or greater, were introduced. For the pressure decrease the system was simply exhausted at intervals by lowering the mercury cutout which separated the vacuum system from the mercury vapor and the Hyper Vac pumps. Because of the small pressure changes the time required to reach equilibrium was about 2 min. Second readings of both the McLeod and the potentiometer were constant. The resulting calibration curves for the 7 gases are shown in Fig. 3. Each of these curves represents four calibrations for both increase and decrease of pressure from 10^{-6} mm to 10^{-1} mm Hg. The same gas was not used for any two successive calibrations, but rather the order of calibration of the gases was chosen at random.

A linear relationship between energy supplied to the filament, expressed as current, voltage, or resistance, and pressure in the Knudsen range has been observed by a number of investigators (*11, 14, 15*). According to Farkas and Melville (*15*), the energy from a fine wire at low pressure is dissipated in three ways: conduction by the gas, radiation, and conduction along the leads. These quantities are related to the energy input in the wire by the relationship

$$k_1V^2 = T_ek_2 + T_ek_3f(p),$$

where k_1V^2 is the energy input, k is a constant, and V represents voltage; T_ek_2 is the heat loss by conduction along the leads and by radiation which is proportional to the excess temperature T_e of the filament over the surroundings; and $T_ef(p)k_3$ is the energy loss by conduction. It follows that

$$k_1V_0^2 = T_ek_2,$$

where V_0 = voltage required for balancing when the pressure is zero.

$$(V^2 - V_0^2)/V_0^2 = (k_3/k_2)f(p).$$

Hence, these authors state that $f(p)$ is accurately linear up to a pressure of 0.1 mm Hg. Fig. 4 is a plot of this relationship from the data of these calibrations. It is evident that exact linearity does not exist. It might be pointed out that the filament and heating current were not of the specifications used by another of the investigators who claimed this relationship. Von Ubisch (*11*) recommended a 0.01 mm tungsten filament heated sufficiently to maintain a difference in temperature between wire and wall of 100° C. In a previous experiment with a platinum filament it was observed that an increase in heating current produced a more nearly linear relationship. However, since the heating current in these calibrations was sufficient to

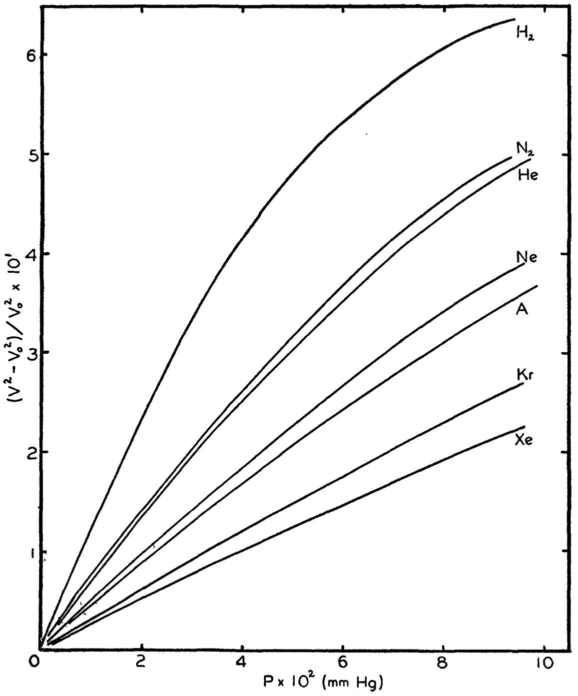

FIG. 4. Calibration curves showing nonlinearity between voltage and pressure.

raise the temperature of the filament to about 220° and the wall temperature was maintained at 0° C, this difference in the wire size hardly explains this deviation from the expected results.

Von Ubisch (*6*) introduced the manometric constant f in his work with the Pirani gauge. This is defined as

$$f = \lambda_{\text{air}}/\lambda_{\text{gas}},$$

where λ is the coefficient of molecular heat conduction. As a result of several identities it is concluded that for the molecular region below 0.1 mm Hg for a 0.01 mm wire, this condition is simply

$$f = p_g/p_a.$$

The values of f in Table 1 are taken directly from the above reference. The author states that f is influenced by changes of the accommodation coefficient and also to some extent by changes in temperature. Hence the values listed are only approximate. The errors should not be in excess of 10% for hydrogen and considerably smaller for the heavier gases.

Because of the deviation in the dimensions of the filament and nonlinearity of the calibration curves for these gases, only an approximate comparison can be made with the values quoted. Since air was not used as a calibrating agent, the ratios are based on nitrogen. The corresponding values on the basis of air would be slightly higher. It will be noted that two values for each gas are given. Linearity does not exist beyond 0.025 mm Hg; hence, one value for f is given in this region, and a second is given at the extreme pressure of the gas, except for hydrogen, at 0.1 mm. This latter value—namely, p_g/p_{N_2}—is obtained by comparing the the pressures at that point at which the voltage reading for the two gases is identical. At this higher value of the pressure the percentage deviation is considerably less than in the region of 0.025 mm.

TABLE 1

Gas	f (*6*)	Ratio $(dV/dp)_{N_2}/(dV/dp)_g$ 0–0.025 mm	% Deviation	P_g/P_{N_2} $p_g =$ 0.1 mm	% Deviation
H_2	0.65	0.60	8.9	0.57	12.3
Air	1.00				
N_2		1.00			
He	1.06	1.06	0.0	1.04	1.9
Ne	1.35	1.51	11.9	1.46	8.2
A	1.60	1.64	2.5	1.64	2.5
Kr	2.29	2.22	3.1	2.31	0.9
Xe		2.74	—	2.92	—

It appears evident that a Pirani gauge of simple design can be constructed which is suitable for use in the region from 10^{-4} mm to 10^{-1} mm Hg. For accurate pressure readings it is necessary to calibrate the gauge with each gas used and for the pressure range to be considered.

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