

For example, if A were a gas with coordinates P (pressure) and V (volume) and obeying Boyle's law, and if C were a similar gas with coordinates P'' and V'' , Eq. (1-1) would be

$$PV - P''V'' = 0.$$

Thermal equilibrium between system B , with coordinates Y' , X' , and system C is similarly denoted by the relation

$$f_{BC}(Y', X'; Y'', X'') = 0, \quad (1-2)$$

where f_{BC} may be quite different from f_{AC} but is also assumed to be a well-behaved function.

Suppose Eqs. (1-1) and (1-2) are solved for Y'' ; then

$$Y'' = g_{AC}(Y, X, X''),$$

and

$$Y'' = g_{BC}(Y', X', X''),$$

or

$$g_{AC}(Y, X, X'') = g_{BC}(Y', X', X''). \quad (1-3)$$

Now, according to the zeroth law, thermal equilibrium between A and C and between B and C implies thermal equilibrium between A and B , which is denoted by a relation among *coordinates of systems A and B only*; thus,

$$f_{AB}(Y, X; Y', X') = 0. \quad (1-4)$$

Since Eq. (1-3) also expresses the same two equilibrium situations, it must agree with Eq. (1-4): that is, it must reduce to a relation among Y , X ; Y' , X' only. The extraneous coordinate X'' in Eq. (1-3) must therefore drop out, and the equation must reduce to

$$h_A(Y, X) = h_B(Y', X').$$

Applying the same argument a second time with systems A and C in equilibrium with B , we get finally, when the three systems are in thermal equilibrium,

$$h_A(Y, X) = h_B(Y', X') = h_C(Y'', X''). \quad (1-5)$$

In other words, a function of each set of coordinates exists, and these functions are all equal when the systems are in thermal equilibrium with one another. The common value t of these functions is the *empirical temperature* common to all the systems.

$$t = h_A(Y, X) = h_B(Y', X') = h_C(Y'', X''). \quad (1-6)$$

The relation $t = h_A(Y, X)$ is merely the equation of an isotherm of system A , such as curve I of Fig. 1-3. If t is given a different numerical value, a different curve is obtained, such as II in Fig. 1-3.

The temperature of all systems in thermal equilibrium may be represented by a number. The establishment of a temperature scale is merely the adoption of a set of rules for assigning one number to one set of corresponding isotherms and a different number to a different set of corresponding isotherms.

1-7 Measurement of Temperature

To establish an empirical temperature scale, we select some system with coordinates Y and X as a standard, which we call a *thermometer*, and adopt a set of rules for assigning a numerical value to the temperature associated with each of its isotherms. To every other system in thermal equilibrium with the thermometer, we assign the same number for the temperature. The simplest procedure is to choose any convenient path in the YX plane, such as that shown in Fig. 1-4 by the dashed line $Y = Y_1$ which intersects the isotherms at points each of which has the same Y coordinate but a different X coordinate. The temperature associated with each isotherm is then taken to be a convenient function of the X at this intersection point. The coordinate X is called the *thermometric property*, and the form of the *thermometric function* $\theta(X)$ determines the temperature scale. There are six important kinds of thermometer, each with its own thermometric property, as shown in Table 1-1.

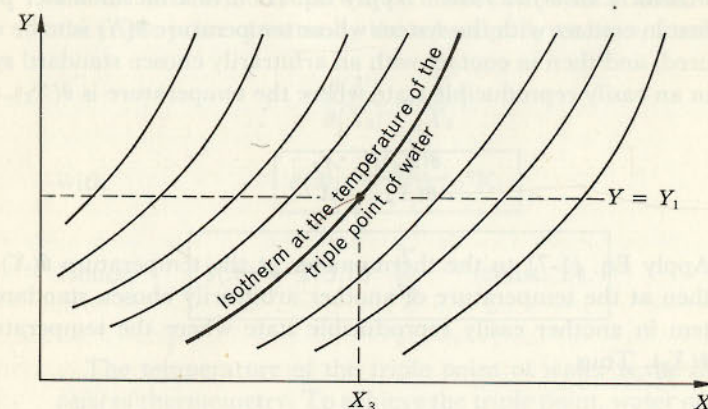


Fig. 1-4 Setting up a temperature scale involves assignment of numerical values to the isotherms of an arbitrarily chosen standard system, or thermometer.

Table 1-1 Thermometers and Thermometric Properties

Thermometer	Thermometric property	Symbol
Gas (const. volume)	Pressure	P
Electric resistor (const. tension)	Electric resistance	R'
Thermocouple (const. tension)	Thermal emf	\mathcal{E}
Helium vapor (saturated)	Pressure	P
Paramagnetic salt	Magnetic susceptibility	χ
Blackbody radiation	Radiant emittance	$\mathcal{E}_{B,\lambda}$

Let X stand for any one of the thermometric properties listed in Table 1-1, and let us *arbitrarily choose* for the temperature common to the thermometer and to all systems in thermal equilibrium with it the following linear function of X :

$$\theta(X) = aX \quad (\text{const. } Y),$$

where a is an arbitrary constant. It follows that two temperatures on this "linear X scale" are to each other as the ratio of the corresponding X 's, or

$$\frac{\theta(X_1)}{\theta(X_2)} = \frac{X_1}{X_2} \quad (1-7)$$

To determine the temperature $\theta(X)$ of a system, either of two procedures may be adopted:

- 1 *Method in use before 1954.* Apply Eq. (1-7) to a thermometer placed first in contact with the system whose temperature $\theta(X)$ is to be measured, and then in contact with an arbitrarily chosen standard system in an easily reproducible state where the temperature is $\theta(X_1)$. Thus

$$\frac{\theta(X_1)}{\theta(X)} = \frac{X_1}{X} \quad (1-8)$$

Apply Eq. (1-7) to the thermometer at the temperature $\theta(X)$, and then at the temperature of another arbitrarily chosen standard system in another easily reproducible state where the temperature is $\theta(X_2)$. Thus

$$\frac{\theta(X_2)}{\theta(X)} = \frac{X_2}{X} \quad (1-9)$$

Subtracting Eq. (1-9) from Eq. (1-8),

$$\frac{\theta(X_1) - \theta(X_2)}{\theta(X)} = \frac{X_1 - X_2}{X},$$

and solving for $\theta(X)$, we get

$$\theta(X) = \frac{\theta(X_1) - \theta(X_2)}{X_1 - X_2} X \quad (\text{const. } Y).$$

Now assign an arbitrary number of "degrees" to the temperature interval $\theta(X_1) - \theta(X_2)$. Then $\theta(X)$ can be calculated from the three measurements X , X_1 , X_2 .

An easily reproducible state of an arbitrarily chosen standard system is called a *fixed point*. Before 1954 there were two fixed points: (1) the temperature at which pure ice coexisted in equilibrium with air-saturated water at one atmosphere pressure (the ice point); and (2) the temperature of equilibrium between pure water and pure steam at one atmosphere pressure (the steam point). The temperature interval between these two fixed points was chosen to be 100 deg. A critical discussion of this abandoned method will be given in Art. 1-12.

- 2 *Method after 1954.* With this method, only one fixed point is chosen, namely, the temperature and pressure at which ice, liquid water, and water vapor coexist in equilibrium, a state known as the *triple point of water*. We choose arbitrarily for the temperature at this fixed point 273.16 degrees Kelvin, abbreviated 273.16°K. (The reason for the use of Kelvin's name will be made clear later.) Thus, designating the triple point of water by the subscript 3, we have, from Eq. (1-7),

$$\frac{\theta(X)}{\theta(X_3)} = \frac{X}{X_3},$$

with

$$\theta(X_3) = 273.16^\circ\text{K}.$$

Hence,

$$\theta(X) = 273.16^\circ \frac{X}{X_3} \quad (\text{const. } Y). \quad (1-10)$$

The temperature of the triple point of water is the *standard fixed point* of thermometry. To achieve the triple point, water of the highest purity is distilled into a vessel depicted schematically in Fig. 1-5. When all air has been removed, the vessel is sealed off. With the aid

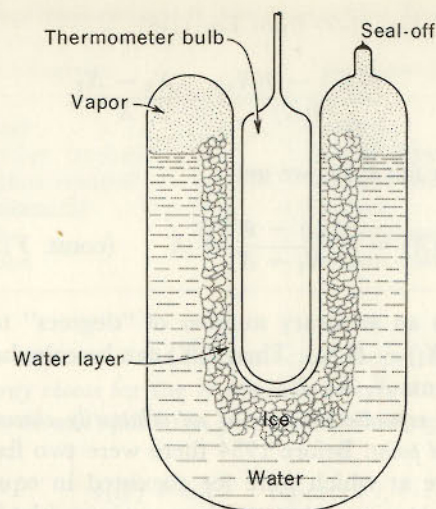


Fig. 1-5 Triple-point cell.

of a freezing mixture in the inner well, a layer of ice is formed around the well. When the freezing mixture is replaced by a thermometer bulb, a thin layer of ice is melted nearby. So long as the solid, liquid, and vapor phases coexist in equilibrium, the system is at the triple point. The actual shape of the apparatus used by the U.S. National Bureau of Standards is shown in Fig. 1-6.

1-8 Comparison of Thermometers

Applying the principles outlined in the preceding paragraphs to the first three thermometers listed in Table 1-1, we have three different ways of measuring temperature. Thus, for a gas at constant volume,

$$\theta(P) = 273.16^\circ \frac{P}{P_3} \quad (\text{const. } V);$$

for an electric resistor,

$$\theta(R') = 273.16^\circ \frac{R'}{R_3};$$

and for a thermocouple,

$$\theta(\mathcal{E}) = 273.16^\circ \frac{\mathcal{E}}{\mathcal{E}_3}.$$

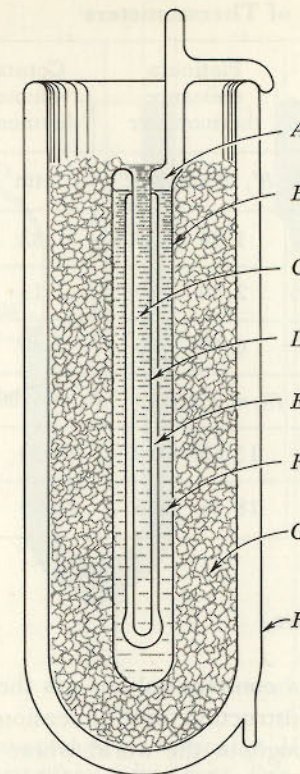


Fig. 1-6 Diagram of the NBS triple-point cell (B, D) in use in an ice bath (G) within a Dewar flask (H). A, water vapor; C, thermometer well; E, ice mantle; F, liquid water.

Now imagine a series of tests in which the temperature of a given system is measured simultaneously with each of the three thermometers. Such a comparison is shown in Table 1-2. The initials NBP stand for the *normal boiling point*, which is the temperature at which a liquid boils at atmospheric pressure; the letters NMP stand for *normal melting point*, NSP for the *normal sublimation point*, and TP for the *triple point*. The numerical values are not meant to be exact, and 273.16 has been written simply 273. If one compares the θ columns, it may be seen that at any fixed point, except the triple point of water, the thermometers disagree. Even the two hydrogen thermometers disagree slightly, but the variation among gas thermometers may be greatly reduced by using low pressures, so that a gas thermometer has been chosen as the standard thermometer in terms of which the empiric temperature scale is defined.

Table 1-2 Comparison of Thermometers

Fixed point	Copper-constantan thermocouple		Platinum resistance thermometer		Constant-volume H ₂ thermometer		Constant-volume H ₂ thermometer	
	\mathcal{E} , mV	$\theta(\mathcal{E})$	R' , ohms	$\theta(R')$	P , atm	$\theta(P)$	P , atm	$\theta(P)$
N ₂ (NBP)	0.73	32.0	1.96	54.5	1.82	73	0.29	79
O ₂ (NBP)	0.95	41.5	2.50	69.5	2.13	86	0.33	90
CO ₂ (NSP)	3.52	154	6.65	185	4.80	193	0.72	196
H ₂ O (TP)	$\mathcal{E}_3 = 6.26$	273	$R_3 = 9.83$	273	$P_3 = 6.80$	273	$P_3 = 1.00$	273
H ₂ O (NBP)	10.05	440	13.65	380	9.30	374	1.37	374
Sn (NMP)	17.50	762	18.56	516	12.70	510	1.85	505

1-9 Gas Thermometer

A schematic diagram of a constant-volume gas thermometer is shown in Fig. 1-7. The materials, construction, and dimensions differ in the various bureaus and institutes throughout the world where these instruments are used and depend on the nature of the gas and the temperature range for which the thermometer is intended. The gas is contained in the bulb *B* (usually made of platinum or a platinum alloy), which communicates with the mercury column *M* through a capillary. The volume of the gas is kept constant by adjusting the height of the mercury column *M* until the mercury level just touches the tip of a small pointer in the space above *M*, known as the *dead space* or *nuisance volume*. The mercury column *M* is adjusted by raising or lowering the reservoir. The difference in height *h* between the two mercury columns *M* and *M'* is measured when the bulb is surrounded by the system whose temperature is to be measured, and when it is surrounded by water at the triple point.

The various values of the pressure must be corrected to take account of the following sources of error:

- 1 The gas present in the dead space (and in any other nuisance volumes) is at a temperature different from that in the bulb.
- 2 The gas in the capillary connecting the bulb with the manometer has a temperature gradient; i.e., it is not at a uniform temperature.

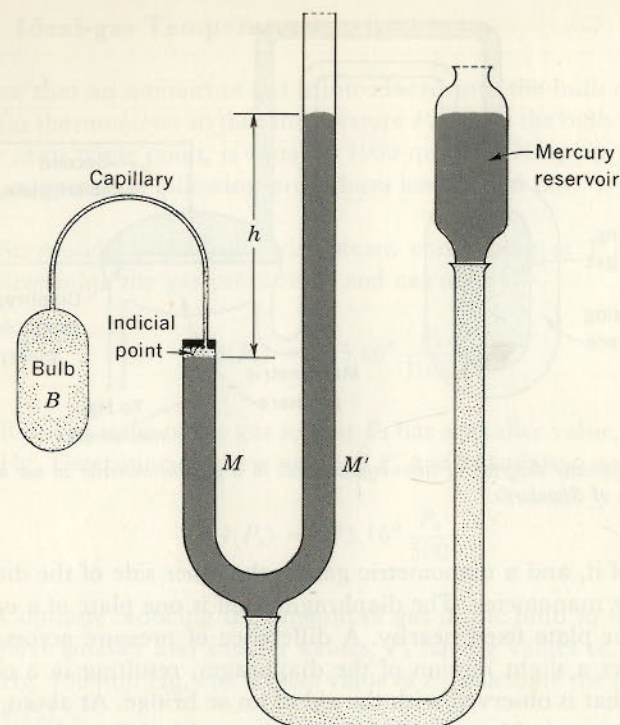


Fig. 1-7 Simplified constant-volume gas thermometer. Mercury reservoir is raised or lowered so that meniscus at left always touches indicial point. Bulb pressure equals *h* plus atmospheric pressure.

- 3 The bulb, capillary, and nuisance volumes undergo changes of volume when the temperature and pressure change.
- 4 If the diameter of the capillary is comparable with the mean free path of the molecules of the gas, a pressure gradient exists in the capillary (Knudsen effect).
- 5 Some gas is adsorbed on the walls of the bulb and capillary, the lower the temperature, the greater the adsorption.
- 6 There are effects due to temperature and compressibility of the mercury in the manometer.

Many great improvements in the design of gas thermometers have been made in recent years. Two of these are depicted schematically in Fig. 1-8. Instead of the thermometric gas in the bulb communicating directly with the mercury in the manometer, there are two separate volumes of gas: the thermometric gas, which goes as far as a diaphragm and exerts a pressure

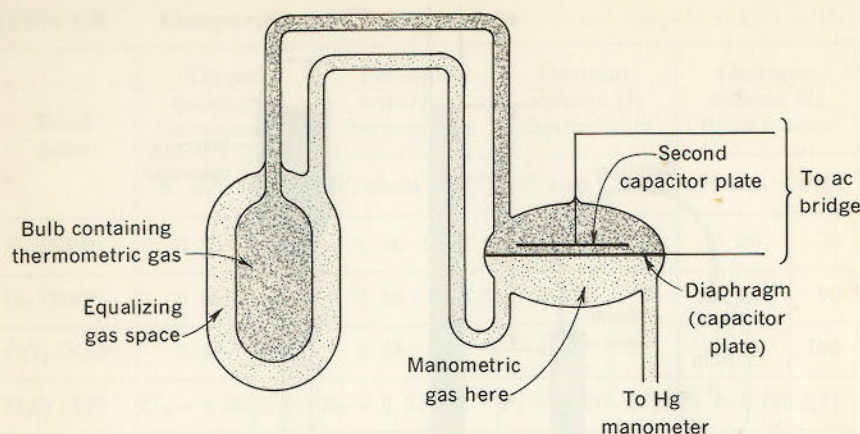


Fig. 1-8 Schematic diagram of two improvements in a gas thermometer in use at the U.S. National Bureau of Standards.

on one side of it, and a manometric gas on the other side of the diaphragm leading to the manometer. The diaphragm itself is one plate of a capacitor, with the other plate fixed nearby. A difference of pressure across the diaphragm causes a slight motion of the diaphragm, resulting in a change of capacitance that is observed with the aid of an ac bridge. At about 1 atm, a pressure differential of 1 part per million is detectable. When the diaphragm shows no deflection, the manometric gas pressure is the same as that of the thermometric gas, and a reading of the manometer gives the gas pressure in the bulb.

Another improvement depicted in Fig. 1-8 is an equalizing gas space surrounding the bulb. The manometric gas is allowed to fill this space. At the moment when a manometer reading is made, there is no net force tending to alter the dimensions of the bulb, and therefore no correction need be made for a variation of bulb volume with pressure.

The greatest improvements have been made in the mercury manometer. The mercury meniscus in each tube is made very flat by widening the tubes, since the dead space does not depend on this width as it did in the older instrument depicted in Fig. 1-7. The position of a mercury meniscus is obtained by using it as one plate of a capacitor, with the other being fixed nearby, and measuring the capacitance with an ac bridge. Gauge blocks are used to measure the difference in height of the two mercury columns. Pressures can be measured exact to a few ten-thousandths of a millimeter of mercury.

One gas thermometer has been built with a differential pressure diaphragm in the thermometer bulb itself, thereby eliminating the dead space entirely.

1-10 Ideal-gas Temperature

Suppose that an amount of gas is introduced into the bulb of a constant-volume gas thermometer so that the pressure P_3 , when the bulb is surrounded by water at its triple point, is equal to 1000 mm Hg. Keeping the volume V constant, suppose the following procedures are carried out:

- 1 Surrounding the bulb with steam condensing at 1 atm pressure, determine the gas pressure P_s and calculate

$$\theta(P_s) = 273.16^\circ \frac{P_s}{1000}.$$

- 2 Remove some of the gas so that P_3 has a smaller value, say, 500 mm Hg. Determine the new value of P_s and calculate a new value

$$\theta(P_s) = 273.16^\circ \frac{P_s}{500}.$$

- 3 Continue reducing the amount of gas in the bulb so that P_3 and P_s have smaller and smaller values, P_3 having values of, say, 250 mm Hg, 100 mm Hg, etc. At *each* value of P_3 , calculate the corresponding $\theta(P_s)$.
- 4 Plot $\theta(P_s)$ against P_3 and extrapolate the resulting curve to the axis where $P_3 = 0$. Read from the graph

$$\lim_{P_3 \rightarrow 0} \theta(P_s).$$

The results of a series of tests of this sort are plotted in Fig. 1-9 for four different gases in order to measure $\theta(P)$ not only of condensing steam but also of condensing sulfur. The graph conveys the information that, although the readings of a constant-volume gas thermometer depend upon the nature of the gas at ordinary values of P_3 , *all gases indicate the same temperature as P_3 is lowered and made to approach zero.*

We therefore define the *ideal-gas temperature* θ by the equation

$$\theta = 273.16^\circ \lim_{P_3 \rightarrow 0} \left(\frac{P}{P_3} \right) \quad (\text{const. } V). \quad (1-11)$$

Although the ideal-gas temperature scale is independent of the properties of any one particular gas, it still depends on the properties of gases in general.

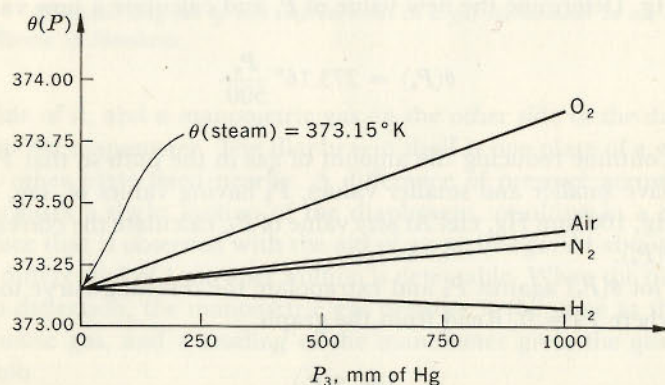
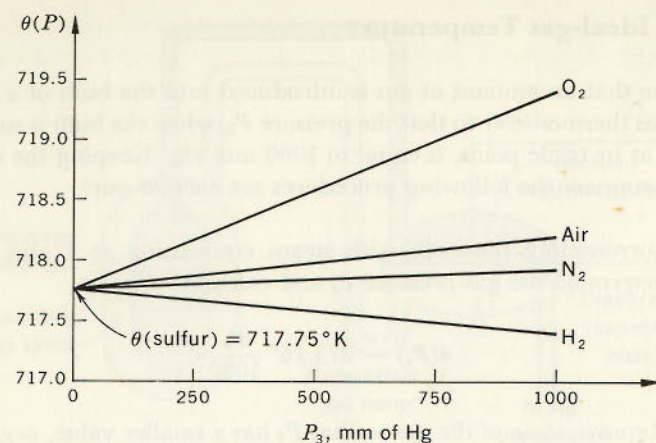


Fig. 1-9 Readings of a constant-volume gas thermometer for the temperature of condensing steam and for that of condensing sulfur, when different gases are used at various values of P_3 .

Helium is the most useful gas for thermometric purposes for two reasons. At high temperatures helium does not diffuse through platinum, whereas hydrogen does. Furthermore, helium becomes a liquid at a temperature lower than any other gas, and therefore a helium thermometer may be used to measure temperatures lower than those which can be measured with any other gas thermometer.

The lowest ideal-gas temperature that can be measured with a gas thermometer is about 0.5°K , provided that low-pressure He^3 is used. The temperature $\theta = 0$ remains as yet undefined. In Chap. 7 the Kelvin temperature scale, which is independent of the properties of any particular substance, will be developed. It will be shown that, in the temperature region in which a gas thermometer may be used, the ideal-gas scale and the Kelvin scale are identical. In anticipation of this result, we write $^\circ\text{K}$ after an ideal-gas tem-

perature. It will also be shown in Chap. 7 how the absolute zero of temperature is defined on the Kelvin scale. Until then, the phrase "absolute zero" will have no meaning. It should be remarked that the statement, found in so many textbooks of elementary physics, that, at the temperature $T = 0$, all molecular activity ceases is entirely erroneous. First, such a statement involves an assumption connecting the purely macroscopic concept of temperature and the microscopic concept of molecular motion. If we want our theory to be general, this is precisely the sort of assumption that must be avoided. Second, when it is necessary in statistical mechanics to correlate temperature to molecular activity, it is found that classical statistical mechanics must be modified with the aid of quantum mechanics and that, when this modification is carried out, the molecules of a substance at absolute zero have a *finite* amount of kinetic energy, known as the *zero-point energy*.

1-11 Celsius Temperature Scale

The Celsius temperature scale employs a degree of the same magnitude as that of the ideal-gas scale, but its zero point is shifted so that the Celsius temperature of the triple point of water is 0.01°C , abbreviated 0.01°C . Thus, if t denotes the Celsius temperature,

$$t = \theta - 273.15^\circ. \quad (1-12)$$

Thus, the Celsius temperature t_s at which steam condenses at 1 atm pressure is

$$t_s = \theta_s - 273.15^\circ,$$

and reading θ_s from Fig. 1-9,

$$\begin{aligned} t_s &= 373.15^\circ - 273.15^\circ \\ &= 100.00^\circ\text{C}. \end{aligned}$$

The accurate measurement of temperature with a gas thermometer requires months of painstaking laboratory work and mathematical computation and when completed becomes an international event. Such work is published in a physical journal and eventually is listed in tables of physical constants. The temperatures of the normal boiling points (NBP) and normal melting points (NMP) of a number of materials have been measured, and the results are tabulated in Table 1-3. The fixed points designated in the

table as basic are used to calibrate other thermometers in a manner that will be described in Art. 1-14.

Table 1-3 Temperatures of Fixed Points

Fixed points		Temp., °C	Temp., °K
Standard	Triple point of water	0.01	273.16
Basic	NBP of hydrogen (hydrogen point)	-252.88	20.26
	NBP of oxygen (oxygen point)	-182.97	90.17
	Equilibrium of ice and air-saturated water (ice point)	0.00	273.15
	NBP of water (steam point)	100.00	373.15
	NMP of zinc (zinc point)	419.51	692.66
	NMP of antimony (antimony point)	630.50	903.65
	NMP of silver (silver point)	961.90	1235.05
	NMP of gold (gold point)	1064.5	1337.65
Secondary	NBP of helium	-268.93	4.22
	NBP of neon	-246.09	27.09
	NBP of nitrogen	-195.81	77.35
	NMP of mercury	-38.86	234.29
	Transition point of sodium sulfate	32.38	305.53
	NBP of naphthalene	217.96	491.11
	NMP of tin	231.913	505.00
	NBP of benzophenone	305.90	579.05
	NMP of cadmium	320.90	594.05
	NMP of lead	327.30	600.45

Notice that among the basic fixed points there are two normal boiling points, those of oxygen and of water. The normal boiling point is the temperature at which a liquid and its vapor remain in equilibrium when the vapor exerts a pressure of exactly 1 atm. Should the pressure depart from 1 atm by only 1 cm of mercury, the temperature change would be several tenths of a degree. It is necessary therefore to have elaborate controls on the vapor pressure to keep it constant to within a fraction of a millimeter of mercury. Such controls are available at the major bureaus of standards, but not in the average laboratory.

A normal melting (or freezing) point is defined also at 1 atm pressure. A change of pressure of 1 cm of mercury on a solid, however, produces a change in melting point of only about 0.00001 deg, and therefore no precautions need be taken. As a result, there is a growing tendency to eliminate all boiling points as fixed points and to retain only melting points and triple points.

1-12 Electric Resistance Thermometry

When the resistance thermometer is in the form of a long, fine wire, it is usually wound around a thin frame constructed so as to avoid excessive strains when the wire contracts upon cooling. In special circumstances the wire may be wound on or embedded in the material whose temperature is to be measured. In the very-low-temperature range, resistance thermometers often consist of small carbon-composition radio resistors or a germanium crystal doped with arsenic and sealed in a helium-filled capsule. These may be bonded to the surface of the substance whose temperature is to be measured or placed in a hole drilled for that purpose.

It is customary to measure the resistance by maintaining a known constant current in the thermometer and measuring the potential difference across it with the aid of a very sensitive potentiometer. A typical circuit is shown in Fig. 1-10. The current is held constant by adjusting a rheostat so that the potential difference across a standard resistor in series with the thermometer, as observed with a monitoring potentiometer, remains constant.

The platinum resistance thermometer may be used for very accurate work within the range of -253 to 1200°C . The calibration of the instrument involves the measurement of R'_{Pt} at various known temperatures and the representation of the results by an empiric formula. In a restricted range, the following quadratic equation is often used:

$$R'_{Pt} = R'_0(1 + At + Bt^2),$$

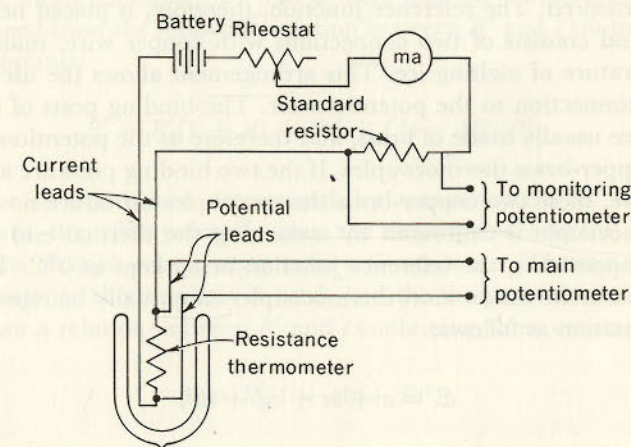


Fig. 1-10 Circuit for measuring the resistance of a resistance thermometer through which a constant current is maintained.