F U N D A M E N T A L S   O F   T H E R M O M E T R Y

PART I

by Henry E. Sostmann

1: THE ABSOLUTE OR THERMODYNAMIC KELVIN, TEMPERATURE SCALE

Temperature is a measure of the hotness of something. For a measure to be rational (and useful between people), there must be agreement on a scale of numerical values (the most familiar of which is the Celsius or Centigrade Scale), and on devices for interpolating between the defining values.

The only temperature scale with a real basis in nature is the Thermodynamic Kelvin Temperature Scale (TKTS), which can be deduced from the First and Second laws of Thermodynamics. The low limit of the TKTS is absolute zero, or zero Kelvin, or 0K (without the mark), and since it is linear by definition, only one nonzero reference point is needed to establish its slope. That reference point was chosen, in the original TKTS, as 273.15K, or 0°C.

0°C is a temperature with which we all have a common experience. It is the temperature at which water freezes, or, coming from the other side, ice melts; at which water exists under ideal conditions as both a liquid and a solid under atmospheric pressure. In 1954 the reference point was changed to a much more precisely reproducible point, 0.01°C. This is known as the triple point of water, and is the temperature at which water exists simultaneously as a liquid and a solid under its own vapor pressure. The triple point of water will be the subject of extended discussion in a later article in this series of articles. It is the most important reference point in thermometry.

The unit of temperature of the TKTS is the Kelvin, abbreviated "K". The temperature interval °C is identically equal to the temperature interval K, and °C or K (the latter without the ° symbol) may be used also to indicate a temperature interval. The difference between 1°C and 2°C is 1K or 1°C, but the temperature 1°C = the temperature 274.15K.

Measurements of temperature employing the TKTS directly are hardly suitable for practicable thermometry. Most easily used thermometers are not based on functions of the First and Second Laws. The practicable thermometers that will be discussed later in this series of articles depend upon some function that is a repeatable and single-valued analog of, or consequence of, temperature, and they are used as interpolation devices of utilitarian temperature scales (such as the International Temperature Scale) which are themselves artifacts. The main purpose for the realization of the TKTS is to establish relationships between the Thermodynamic Scale of nature and the practical scales and thermometers of the laboratory or of industry, so that measurements made by non-thermodynamic means can be translated into terms of the TKTS, and rational temperature scales can be constructed on a basis related to realizable physical phenomena.

There exists in nature a number of what are called thermometric fixed points. These are physical states in which some pure material exists in two or three of the three possible phases simultaneously, and temperature is constant.

A two-phase equilibrium is represented by the earlier example of the freezing point of water, or, more properly, the coexistence of liquid and solid water. For this equilibrium to represent a constant temperature, $0^{\circ}C$, pressure must be specified, and the specification is a pressure of 1 standard atmosphere, 10 1325 Pascal. (A two-phase fixed point at 1 standard atmosphere is called the "normal" point). The variation due to pressure from the defined temperature of a liquid-solid equilibrium is not large (which is not to say that it may not be significant). The freezing point of water is reduced approximately 0.01K for an increase of pressure of 1 atmosphere. The variation due to pressure for a liquid-vapor equilibrium is relatively very large.

A three-phase equilibrium is represented by the triple point of water, the coexistence of liquid and solid water under its own vapor pressure, at $0.01^{\circ}C$. Because all three possible phases are determined by the physical state, it is generally possible to realize a triple point more accurately than a two-phase point.

This may be seen from the Phase Rule of Gibbs:

$$P - C - 2 = F \qquad\qquad\qquad \text{Eq.1}$$

where P is an integer equal to the numiler of phases present, C is the number of kinds of molecule present (for an ideally pure material, C = 1) and F is an integer giving the number of degrees of freedom. Obviously, for the two-phase equilibrium there is one degree of freedom, pressure, and for the three-phase equilibrium F = 0; that is, the temperature is independent of any other factor. Fig.1 illustrates one, two and three-phase equilibria.
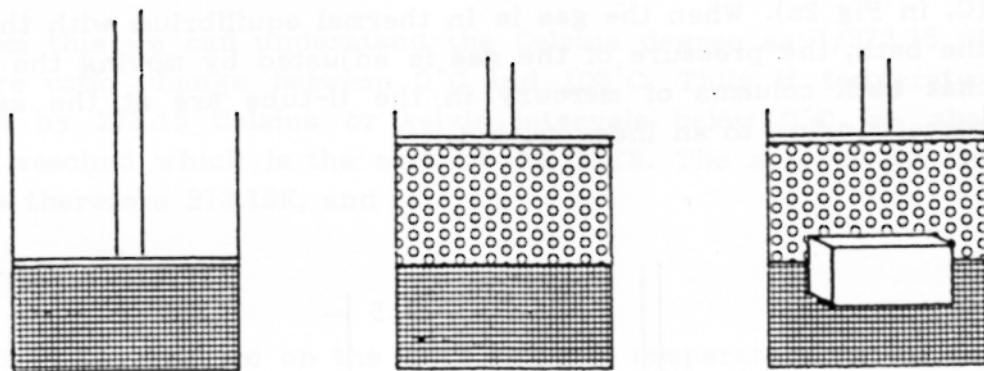
la	2a	3a
P = 1	P = 2	P = 3
C = 1	C = 1	C = 1
F = 3	F = 2	F = 0

Fig. 1: The Phase Rule of Gibbs. P = the number of phases present; C = the number of components (1 for a pure material); F = the degrees of freedom. la is uncontrolled. lb is a melt or freeze point. 1c is a triple point.

A typical device for realizing the TKTS is the helium gas thermometer, since the vapor pressure of an ideal gas is a thermodynamic function (or rather a statistical mechanical function, which for the purpose is the same thing). The transfer function of a gas thermometer may be chosen to be the change in pressure of a gas kept at constant volume, or the change in volume of a gas kept at constant pressure. Since it is easier to measure accurately change in pressure than it is to measure change in volume, constant-volume gas thermometers are more common in use than constant-pressure gas thermometers.

A rudimentary gas thermometer is shown in Fig 2. Its operation will be illustrated by using it to show that the zero of the TKTS is 273.15K below the temperature of the normal freezing point of water, 0' on the Celsius Scale.

Fig. 2 shows a cylindrical bulb of constant volume, connected by tubing defined as constant-volume, to a U-tube manometer. A second connection to the manometer leads to a reservoir of mercury, which contains a plunger, P, by means of which the column height of the manometer may be varied. The constant-volume bulb and tubing contain an ideal gas. The bulb is first surrounded by an equilibrium mixture of ice and water (C, in Fig 2a). When the gas is in thermal equilibrium with the slurry in the bath, the pressure of the gas is adjusted by moving the plunger so that both columns of mercury in the U-tube are at the same height, corresponding to an index mark 1.
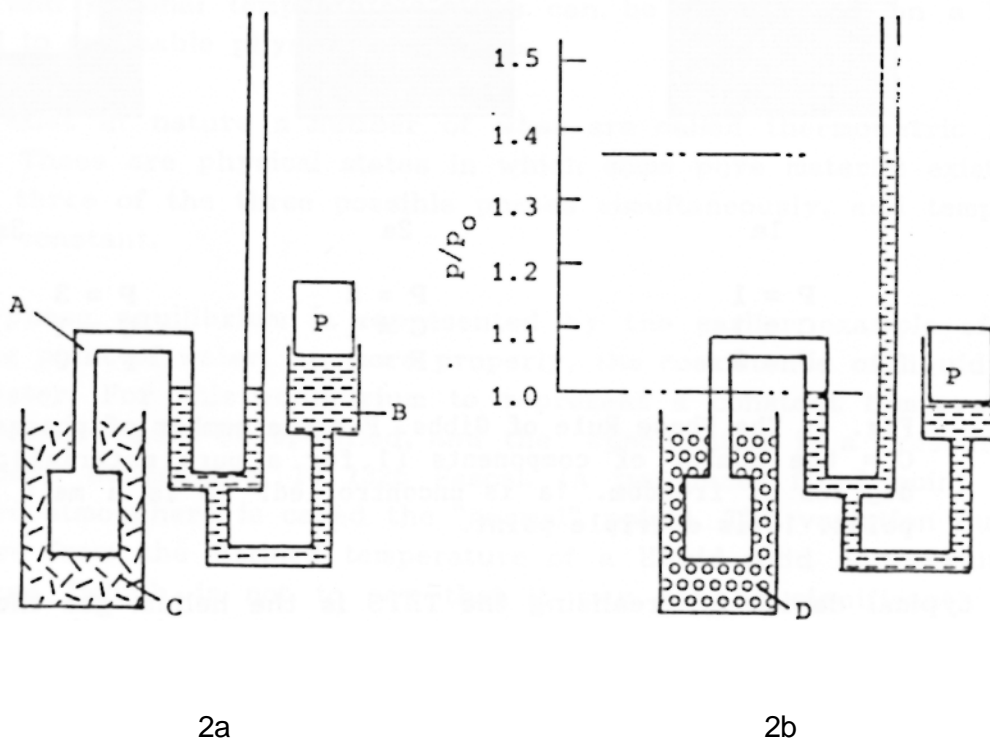

2a   2b

Fig.2: A rudimentary gas thermometer. A = helium gas. B = mercury,
C = water + ice (0 C), D = water + steam (100'C), P = a plunger for
adjusting mercury level.

Next, the ice bath is removed and replaced with a bath containing boiling water, or more correctly, an equilibrium mixture of liquid and vapor water at a pressure of 1 standard atmosphere, (D, in Fig 2b). As the manometric gas is heated by the boiling water it expands, and the mercury in the manometer is displaced. The plunger is actuated to re-position the surface of the mercury in the left leg at the index mark 1, restoring the criterion of constant volume in the closed gas system, a condition shown in Fig 2b. However the mercury in the right, open leg is not now at the index mark 1, but measurably higher. In fact, the difference in heights indicates that the pressure of the enclosed gas at the boiling point is 1.366099 times the pressure at the freezing point. We can then calculate:

$$(100°0 – 0°C)/(1.366099 – 1) = 273.15 \qquad\qquad \textbf{Eq. 2}$$

and from this we can understand the Celsius degree as 1/273.15 of the pressure ratio change between $0°C$ and $100°C$. Thus if temperature is reduced by 273.15 Celsius or Kelvin intervals below $0°C$, an absolute zero is reached which is the zero of the TKTS. The zero of the Celsius Scale is therefore 273.15K, and

$$T = t + 273.15 \qquad\qquad \textbf{Eq.3}$$

where T is temperature on the TKTS and t is temperature on the Celsius Scale. Note that the temperature interval and the zero of the TKTS have been defined without reference to the properties of any specific sub-stance.

All constant volume gas thermometer measurements can be expressed in terms of the equation

$$P_1 / P_2 = (T_1 - T_0) / (T_2 - T_0) \qquad\qquad \textbf{Eq.4}$$

where the Ts are temperatures on the TKTS, the natural temperature Scale, and the. T_0s are the zero of that Scale.

This relationship assumes an ideal gas. The reader will have observed that the gas thermometer reflects Charles' or Boyle's law, if the pressure or the volume of the gas, respectively, be held constant. An ideal gas, is a gas whose behavior can be predicted exactly from Boyle's or Charles' Law, which obeys it through all ranges of temperature or pressure, and where the relationship between concentration (n/V), absolute temperature and absolute pressure is

$$(n/V)(T/P) = 1/R = a\ constant \qquad\qquad \textbf{Eq.5}$$

more commonly written as

$$PV = nRT \qquad\qquad \textbf{Eq.6}$$

where R is the gas constant, identical for all ideal gases. R = 0.082053, and is known to about 30ppm.

A second condition is that there be no intermolecular forces acting, thus the internal energy, V, does not depend on the molecular distances, and

$$(dE / dV)_T = 0 \hspace{6cm} \text{Eq.7}$$

Unfortunately there is no real ideal gas, and the uncertainty of 30ppm is a large number. Helium comes closest, carbon dioxide varies most widely from ideality. However real gases approach ideality as their pressures are reduced, reflecting a reduction in density. Since it is not possible to measure the change in pressure of a gas at zero pressure (or the change in volume of a gas at zero volume) the requirement for an ideal gas is approached by making a number of measurements at a number of pressures and extrapolating to zero pressure. Such a system of measurements is shown in Fig. 3. Regardless of the nature of the gas, all gas thermometers at the same temperature approach the same reading as the pressure of the gas approaches zero.
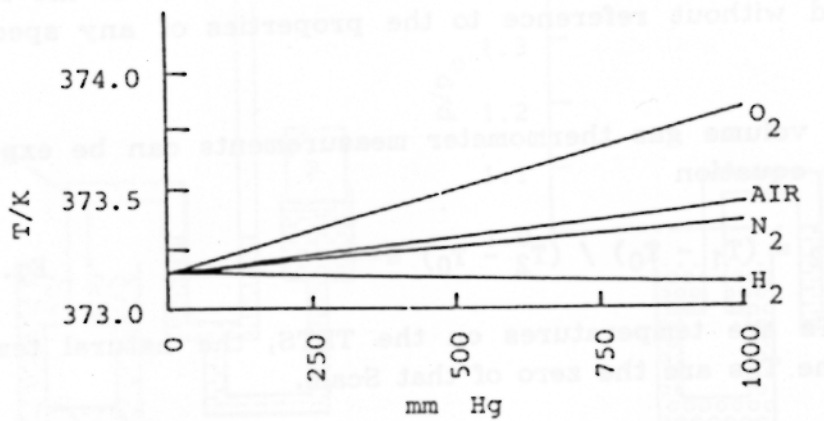

Fig 3: Pressure ratios of various gases at various pressures at the condensation point of steam.

Several authors have proposed modifications of the ideal gas law to account for the non-ideality of real gases. One which is much used, that of Clausius, is the virial equation, which is a series expansion in terms of the density of the gas, and is written:

$$PV = nRT\left(1 + \frac{nB_v}{V} + \frac{n^2 C_v}{V^2} + \frac{n^3 D_v}{V^3} + \ldots \right) \hspace{3cm} \text{Eq.8}$$

where the coefficients B, C, D, etc., are called the second, third, fourth, etc., volume virial coefficients, and are constants for a given gas at a given temperature. Over the usual range of gas densities in gas thermometry, it is seldom necessary to go beyond the second virial coefficient.

The departure of real gases from ideality is only one of the problems of accurate gas thermometry. A second is the purely mechanical matter of dead space. There must be a real connection to convey the pressure from the bulb to the manometer. It is inconvenient to locate the bulb and the manometer in the same thermostatted enclosure, and a common practice is to use two separate enclosures, each carefully thermostatted. Fig. 4 is a modification of Fig. 2 to illustrate this configuration.
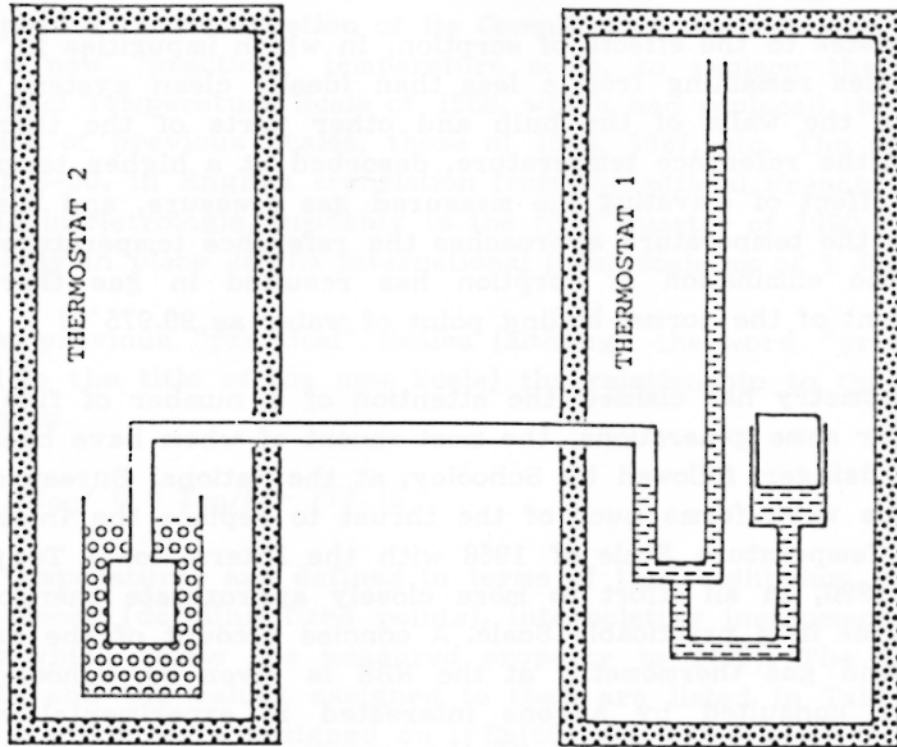

Fig.4: Thermostatted gas thermometer. The U-tube manometer and the gas bulb are separately kept at constant temperature; the (long, perhaps many meters) capillary is not.

The price paid is that there is a capillary tube, generally of some length, which goes through the wall of each of the two thermostats and whose temperature is essentially uncontrolled. The solutions are care and compromise. The bulb volume can be made as large as possible relative to the capillary volume. The temperature distribution along the capillary length can be measured at suitable intervals. The capillary volume can be kept small by providing a capillary of small diameter, but not so small as to introduce thermo molecular pressures where the tube passes through a temperature gradient, or, conversely, a correction for thermo molecular pressure can be made.

A third obvious problem is that of the thermal expansion of the materials of construction. An ideal constant-volume gas thermometer assumes that only the contained gas is subject to thermal expansion, while in reality the whole system is subject to temperature changes, which must be known or estimated, and for which correction must be made.

A fourth correction required is for the hydrostatic head pressure of the gas in the system, including that of the gas column itself.

A fifth relates to the effects of sorption, in which impurities in the gas, or impurities remaining from a less than ideally clean system, are absorbed on the walls of the bulb and other parts of the thermometer system at the reference temperature, desorbed at a higher temperature, with the effect of elevating the measured gas pressure, and then reabsorbed as the temperature approaches the reference temperature. Attention to the elimination of sorption has resulted in gas thermometry measurement of the normal boiling point of water as 99.975°C!

Gas thermometry has claimed the attention of a number of fine experimenters for some generations, the most recent of whom have been Guildner and Edsinger, followed by Schooley, at the National Bureau of Standards. This work forms much of the thrust to replace the International Practical Temperature Scale of 1968 with the International Temperature Scale of 1990, in an effort to more closely approximate thermodynamic temperatures in a practicable Scale. A concise account of the gas thermometer and gas thermometry at the NBS is given by Schooley, and should be consulted by anyone interested in experimental elegance. Schooley provides an example of the accuracy and precision of this work:

Fixed point	Gas therm	IPTS-68	Uncertainty
°C	°C	°C	
Steam pt	99.975	100.000	±0.005
Tin pt	231.924	231.9681	±0.015
Zinc pt	419.514	419.58	±0.03

With the conclusion of work in preparation for ITS-90, gas thermometry is considered to be a finished matter at the NBS. The gas thermometer itself, which should have been preserved as a national shrine or monument, is now in the process of dismemberment.

As a generality, gas thermometry has led the development of thermodynamic values of the thermometric fixed points, and a variety of other methods have been used largely to check its accuracy and consistency. These include acoustic thermometry, dielectric-constant gas thermometry, noise thermometry and radiation thermometry, each appropriate to a portion of the range of the temperature Scale.