Lecture # 3

ES0201A

Temperature and the Zeroth Law of Thermodynamics

Although we are familiar with temperature as a measure of "hotness" or "coldness", it is not easy to give an exact definition for it. Based on our physiological sensations, we express the level of temperature qualitatively with the words like freezing cold, cold, warm, hot, and red-hot. However, we cannot assign numerical values to temperatures based on our sensations alone. Furthermore, our senses may be misleading. A metal chair, for example, will feel much colder than a wooden one even when both are at the same temperature.

Fortunately, several properties of materials change with temperature in a repeatable and predictable way, and this forms the basis for accurate temperature measurement. The commonly used mercury-in-glass thermometer, for example, is based on the expansion of mercury with temperature. Temperature is also measured by using several other temperature-dependent properties.

It is a common experience that a cup of coffee left on the table eventually cools off and a cold drink eventually warms up. That is, when a body is brought into contact with another body that is at a different temperature, heat is transferred from the body at higher temperature to the one at lower temperature, until both bodies are said to have reached thermal equilibrium. The equality of temperature is the only requirement for thermal equilibrium (Fig. 3.1).

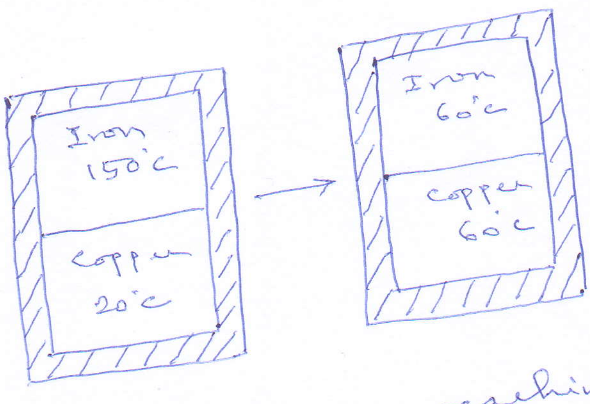

Fig. 3.1 Two bodies reaching thermal equilibrium after being brought into contact in an insulated enclosure

The zeroth law of thermodynamics states that if two bodies are in thermal equilibrium with a third body, they are also in thermal equilibrium with each other. By replacing the third body with a thermometer, the zeroth law can be reworded as two bodies are in thermal equilibrium if both have the same temperature reading even if they are not in contact.

The zeroth law was first formulated by R. H. Fowler in 1931. As the name suggests, its value as a fundamental law was recognized more than half a century after the formulation of the first and the second laws of thermodynamics. It was named the zeroth law since it should have preceded the first and second laws of thermodynamics.

Temperature Scales

The temperature scales used in the SI and in the English system today are the Celsius scale and the Fahrenheit scale, respectively. On the Celsius scale, the ice and steam points were originally assigned the values of 0 and 100°c, respectively. The corresponding values on the Fahrenheit scale are 32 and 212°F. These are often referred to as two-point scales since temperature values are assigned at two different points.

In thermodynamics, it is very desirable to have a temperature scale that is independent of the properties of any substance or substances. Such a temperature scale is called a thermodynamic temperature scale, which is developed later in conjunction with the second law of thermodynamics. The thermodynamic temperature scale in the SI is the Kelvin scale. The temperature unit on this scale is the Kelvin.

The lowest temperature on this scale is absolute zero, or 0 K. Then it follows that only one non-zero reference point needs to be assigned to establish the slope of this linear scale. Using non-conventional refrigeration techniques, scientists have approached absolute zero Kelvin (they achieved 0.000000002 K] in 1989.

The thermodynamic temperature scale in the English system is the Rankine scale. The temperature unit on this scale is the rankine, which is designated by R.

A temperature scale that turns out to be nearly identical to the Kelvin scale is the ideal-gas temperature ~~scale~~ scale. The temperatures on this scale are measured using a constant-volume gas thermometer, which is basically a rigid vessel filled with a gas, usually hydrogen or helium, at low pressure.

This thermometer is based on the principle that at low pressures, the temperature of a gas is proportional to its pressure at constant volume. That is, the temperature of a gas at fixed volume varies linearly with pressure at sufficiently low pressures. Then the relationship between the temperature and the pressure of the gas in the vessel can be expressed as

$$T = a + bP \qquad (3.1)$$

where the values of the constants a and b for a gas thermometer are determined experimentally.

Once a and b are known, the temperature of a medium can be calculated from this relation by immersing the rigid vessel of the gas thermometer into the medium and measuring the gas pressure when thermal equilibrium is established between the medium and the gas in the vessel whose volume is held constant.

An ideal-gas temperature scale can be developed by measuring the pressures of the gas in the vessel at two reproducible points (such as the ice and the steam points) and assigning suitable values to temperatures at those two points. Considering that only one straight line passes through two fixed points on a plane, these two measurements are sufficient to determine the constants a and b in eq. (3.1). Then the unknown temperature T of a medium corresponding to a pressure reading P can be determined from that equation by a simple calculation.

The values of the constants will be different for each thermometer, depending on the type and the amount of gas in the vessel, and the temperature values assigned at the two reference points.

If the ice and steam points are assigned the values 0°c and 100°c, respectively, then the gas temperature scale will be identical to the celsius scale. In this case the value of the constant a (which corresponds to the absolute pressure of zero) is determined to be −273.15°c regardless of the type and the amount of gas in the vessel of the gas thermometer. That is, on a P-T diagram, all the straight lines passing through the data points in this case will intersect the temperature axis at −273.15°c when extrapolated, as shown in Fig. 3.2. This is the lowest temperature that can be obtained by a gas thermometer, and thus we can obtain an absolute gas temperature scale by assigning a value of zero to the constant a in eq. (3.1). In that case, eq. (3.1) reduces to $T = bP$, and thus we need to specify the temperature at only one point to define an absolute gas temperature scale.

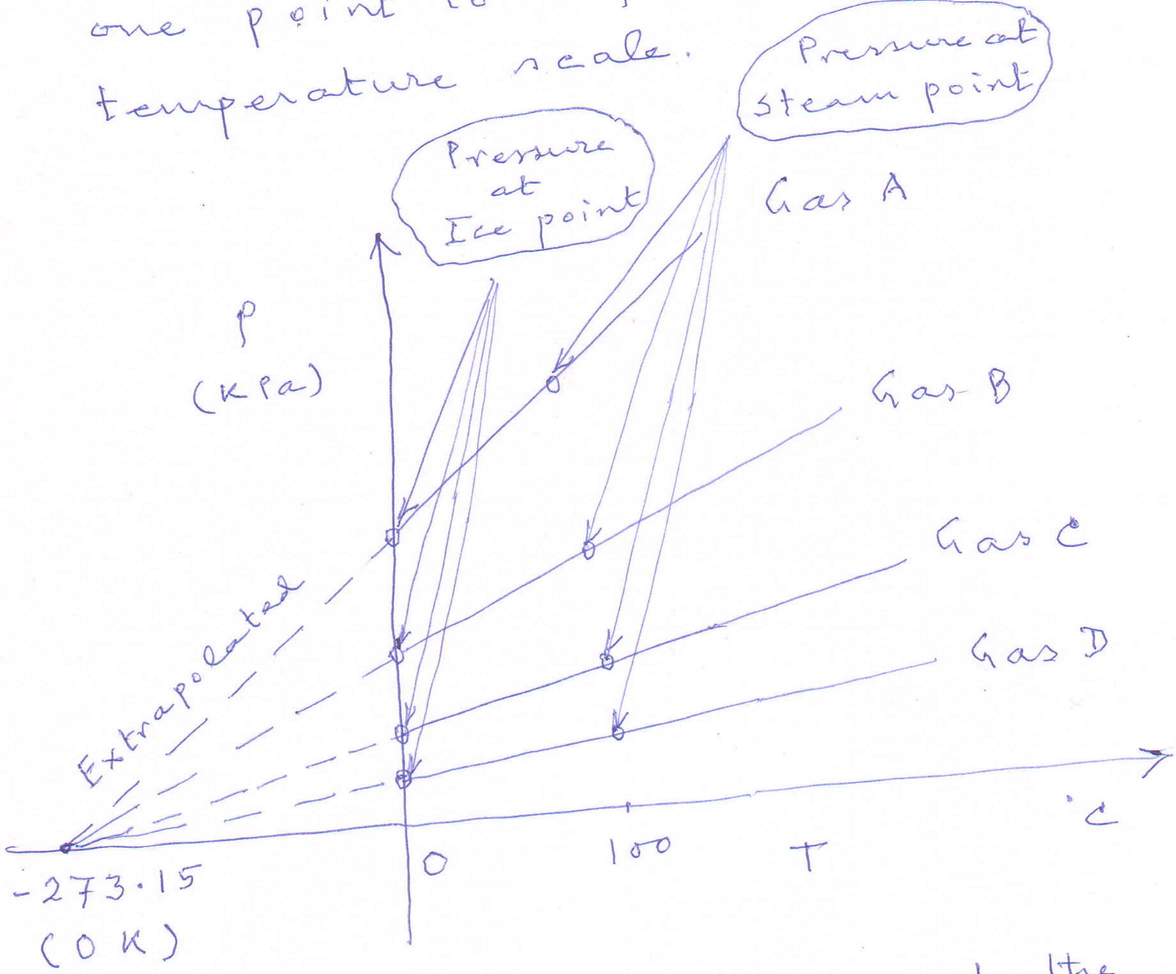

Fig. 3.2 P vs. T plots of the experimental data obtained from a constant-volume gas thermometer using four different gases

In 1954, a single fixed point was chosen as the basis for a new international temperature scale. The state in which ice, liquid water, and water vapour coexist in equilibrium, a state known as the triple point of water, provides the standard reference temperature. The temperature of the triple point of water, which can be very accurately and reproducibly measured, was assigned the value of 273.16 K, corresponding to 0.01°C, in order to maintain the magnitude of a unit of temperature.

Note $T = bP$

At triple-point of water,

$$273.16 = b\, P_{TP_{H_2O}}$$

$$\Rightarrow b = \frac{273.16}{P_{TP_{H_2O}}}$$

Note that P_{TP} of water is 0.611657 kPa.

Therefore, $$\boxed{T = \frac{273.16}{P_{TP_{H_2O}}}\, P}$$

where T is in Kelvin
and P is in kPa.

It should be noted that the absolute gas temperature scale is not a thermodynamic temperature scale, since it cannot be used at very low temperatures (due to condensation) and at very high temperatures (due to dissociation and ionization). However, absolute gas temperature is identical to the thermodynamic temperature in the temperature range in which the gas thermometer can be used. Thus, we can view the thermodynamic temperature scale at this point as an absolute gas temperature scale that utilizes an "ideal" or "imaginary" gas that always act as a low-pressure gas regardless of the temperature. If such a gas thermometer existed, it would read zero Kelvin at absolute zero pressure, which corresponds to −273.15°C on the Celsius scale.