CHAPTER 3
TEMPERATURE

3.1 *Introduction*

During our studies of heat and thermodynamics, we shall come across a number of simple, easy-to-understand terms such as *entropy, enthalpy, Gibbs free energy, chemical potential and fugacity*, and we expect to have no difficulty with these. There is, however, one concept that is really quite difficult to grasp, and that is *temperature*. We shall do our best to understand it in this chapter.

3.2 *Zeroth Law of Thermodynamics*

Perhaps the simplest concept of temperature is to regard it as a potential function whose gradient determines the direction and rate of flow of heat. If heat flows from one body to another, the first is at a higher temperature than the second. If there is no net flow of heat from one body to another, the two bodies are in thermal equilibrium, and their temperatures are equal.

We can go further and assert that

If two bodies are separately in thermal equilibrium with a third body, then they are also in thermal equilibrium with each other.

According to taste, you may regard this as a truism of the utmost triviality or as a fundamental law of the most profound significance. Those who see it as the latter will refer to it as the *Zeroth Law of Thermodynamics* (although the "*zeroth*" does sound a little like an admission that it was added as an afterthought to the other "real" laws of thermodynamics).

We might imagine that the third body is a thermometer of some sort. In fact it need not even be an accurately calibrated thermometer. We insert the thermometer into one of our two bodies (we are not thinking particularly of human bodies here), and it indicates some temperature. Then we insert it into the second body. If it indicates the same temperature as indicated for the first body, then the Zeroth Law asserts that, if we now place our two bodies into contact with each other, there will be no net flow of heat from one to the other. There exists some measure which all three bodies have in common and which dictates that there is no net flow of heat from any one to any other, and the three bodies are in thermal equilibrium. That measure is what we call their temperature.

To some, this will sound like saying :"if A and C are at the same temperature, and if B and C are at the same temperature, then A and B are at the same temperature". Others, of philosophical bent, may want to pursue the concept to greater rigour. In any case, at whatever level of rigour is used, what the Zeroth Law establishes is the existence of some quantity called temperature, but it doesn't really tell us how to define a temperature *scale* quantitatively. It is as if we have established the existence of something called "length" or "mass", but we haven't really specified yet how to measure it or what units to express it in. We could, for example, discuss the concepts of "length" or of "mass" by describing a test to show whether two lengths, or two masses, were *equal*, but without developing any units for expressing such concepts qualitatively. That, I think, is where the Zeroth Law leaves us.

3.3 *Temperature Scales (1)*

In everyday practice, we use either the Celsius or the Fahrenheit temperature scales, depending on what we are used to, or the fashion of the day, or what our Government tells us we should be using. In the Fahrenheit scale, the freezing point of water is 32 $^{\circ}$F and the boiling point is 212 $^{\circ}$F, so that there are 180 F$^{\circ}$ between the two fixed points. In the Celsius scale, the freezing point of water is 0 $^{\circ}$C and the boiling point is 100 $^{\circ}$C, so that there are 100 C$^{\circ}$ between the two fixed points. (When Celsius originally introduced his scale, he set the temperature of boiling water as 0, and the temperature of melting ice as 100. That was reversed within a few years!) The Celsius scale was formerly called "the" centigrade scale, but presumably any scale with 100 degrees between two fixed points could be called a centigrade scale, so we now call it (or are supposed to call it) the Celsius scale.

Conversion is obviously by

$$\mathrm{F} = 1.8\mathrm{C} + 32 \qquad 3.3.1$$

and

$$\mathrm{C} = \frac{\mathrm{F} - 32}{1.8} = \tfrac{5}{9}(\mathrm{F} - 32). \qquad 3.3.2$$

Note that "a temperature of so many degrees on the Fahrenheit scale" is written $^{\circ}$F and "a temperature of so many degrees on the Celsius scale" is written $^{\circ}$C; whereas "a temperature *interval* of so many Fahrenheit degrees" is written F$^{\circ}$ and "a temperature *interval* of so many Celsius degrees" is written C$^{\circ}$. In either case, the degrees symbol ($^{\circ}$) is mandatory.

In scientific work, we generally use the Kelvin temperature scale. The two fixed points on the Kelvin scale are the absolute zero of temperature, which is assigned the temperature 0 K, and the triple point of the water-ice-steam system, which is assigned the temperature 273.16 K. Thus it could reasonably be said that the Kelvin scale is not a centigrade scale, since it doesn't have 100 degrees between its two fixed points. However, the size of the degree on the Kelvin scale is almost exactly the same as the size of the Celsius degree, because the absolute zero of temperature is about –273.15 $^{\circ}$C and the temperature of the triple point is about 0.01 $^{\circ}$C. The definition of the Kelvin scale, however, does not mention the Celsius scale, and therefore, although the size of the degrees is about the same on both scales, this is not inherent in the definition. One might speculate about what might happen in the far distant future if people no longer use the Celsius scale and it is totally forgotten. People then will wonder what possessed us to divide the Kelvin scale into 273.16 divisions between its two fixed points!

It would not be good enough to define the upper fixed point of the kelvin scale as the temperature of "melting ice", because this depends on the pressure. The triple point is the temperature at which ice, water and steam are in equilibrium, and it occurs at a temperature of about 0.01 $^{\circ}$C and exactly 273.16 K, and a pressure of about 610.6 Pa.

The Kelvin scale starts at zero at the lowest conceivable temperature. The kelvin (K) is therefore regarded as a *unit of temperature*, much as a metre is regarded as a unit of length, or a kilogram as a unit of mass. One therefore does not talk about a temperature of so many "degrees Kelvin", any more than one would talk about a length of so many "degrees metre" or a mass of so many "degrees kilogram". When using the Kelvin scale, therefore, we talk simply of a temperature of "280 kelvins" or "280 K". We do not use the word "degree", nor do we use the symbol $^{\circ}$.

In the British Engineering System of units, which is used exclusively in the United States and has never been used in Britain, the Rankine scale is used. The lower fixed point is the absolute zero of temperature, and it is assigned the temperature 0 R, and the size of the rankine is equal to the size of the Fahrenheit degree. Melting ice at 0 $^{\circ}$C has a temperature of 459.67 R, and the triple point has a temperature of 459.688 R.

I doubt whether the Réaumur scale has been used anywhere in the last 50 years, but it has probably been used in the last 100. This had melting ice at 0 $^{\circ}$R and steam at 80 $^{\circ}$R. I mention this only to point out that if you see a temperature given as so many $^{\circ}$R, you might not know whether the Rankine or Réaumur scale is intended! (Strictly, °R would denote degrees Réaumur, while R would denote rankines – but can you trust that?)

In these notes, the Kelvin scale will be the scale that is normally used. There may be occasional use of the Celsius scale, but we shall not use the Fahrenheit, Rankine or Réaumur scales.

3.4 *Temperature Scales (2)*

We now know – by definition – the temperatures at the two fixed points on the Celsius and Kelvin scales. But what about temperatures between the fixed points? We could say that the temperature halfway between the melting point of ice and the boiling point of water is 50 ºC, or we could divide the temperature between the two fixed points into 100 equal intervals. But: What do we mean by "halfway" or by "equal intervals" in such a proposal? This leaves us rather stumped.

Here is one suggestion.

We could construct a glass capillary tube with a bulb at the bottom containing mercury, which also extends a short way up the capillary. We could note the length of the mercury column when the tube was immersed in melting ice and call the temperature 0 ºC, and again when it is in boiling water (100 ºC). We could then divide the length of the tube between these two marks into 100 equal intervals of length, and use that to define our temperature scale. But you may ask: How do we know that mercury expands (relative to glass) uniformly with temperature? Well, it expands uniformly, *by definition*, with temperature *on the mercury-in-glass temperature scale.* Indeed, we can *define* the temperature in the mercury-in-glass scale by

$$t = 100 \times \frac{l_t - l_0}{l_{100} - l_0} \ ^{\circ}\mathrm{C}. \qquad 3.4.1$$

(I am going to use the symbol T in these notes for temperature in *kelvin*. Here I am using t for temperature on the *Celsius* scale.)

If we place the thermometer (for such it is) in a bowl of warm water, and the length of the mercury column is halfway between l_0 and l_{100}, we could say that the temperature of the water in the bowl is, by definition, 50 ºC on the mercury-in-glass scale.

Now let us repeat the experiment with another type of thermometer, using some different property of matter which is also known to vary with temperature. We might choose, for example, to use the electrical resistance R of a length of platinum wire; or the thermoelectric potential difference V that appears when we heat the junction of two different metals; or the pressure P of some gas when it is heated up but kept at constant volume. We could try immersing each of these thermometers into melting ice and boiling water and we could interpolate linearly for intermediate temperatures. Thus, using the resistance of the platinum wire, we could define a platinum resistance temperature scale by

$$t = 100 \times \frac{R_t - R_0}{R_{100} - R_0} \ {}^\circ\mathrm{C}. \tag{3.4.2}$$

Or we could define a thermoelectric temperature scale by

$$t = 100 \times \frac{V_t - V_0}{V_{100} - V_0} \ {}^\circ\mathrm{C}. \tag{3.4.3}$$

Or we could define a constant volume gas temperature scale by

$$t = 100 \times \frac{P_t - P_0}{P_{100} - P_0} \ {}^\circ\mathrm{C}. \tag{3.4.4}$$

But what assurance do we have that all of these temperature scales are the same? What assurance do we have that the resistance of platinum increases linearly on the temperature scale defined by the mercury-in-glass thermometer? What assurance do we have that, when we immerse all of these thermometers in the water that registered 50 ºC for the mercury-in-glass thermometer, they will all register 50 ºC?

The answer is that we have no such assurance.

What we need to do is either choose one particular phenomenon quite arbitrarily to use for our standard temperature scale, or somehow define an *absolute* temperature scale which is absolute in the sense that it is defined independently of the properties of any particular substance. It turns out that it is possible to do the latter, and to define a temperature scale that is absolute and independent of the properties if any particular substance by means of an idealized theoretical concept called a *Carnot Heat Engine*. This imaginary engine uses as its operating medium an equally imaginary substance called an *ideal gas*, and indeed the temperature indicated by a constant volume gas thermometer is identical to the absolute temperature defined by a Carnot engine – provided that the gas used is an ideal gas! The best that can be said for real gases is that, at low pressures, they behave very much like an ideal gas; and indeed if you somehow extrapolate the behaviour or a gas to its behaviour at zero pressure (when there isn't any gas at all!), it would behave exactly like a real gas.

Until we have discussed what are meant by a real gas and by a Carnot engine, all this has served to do is to underline what we said in the Introduction to this chapter – namely that there are a number of relatively easy concepts in thermodynamics, but temperature is not one of them.

If we do eventually understand what a Carnot engine is and we can construct in our minds a definition of what is meant by an absolute temperature scale, there will remain the problem of reproducing such a scale *in practice*. That is the purpose of the International Temperature Scale 1990 (ITS90). On this scale a number of fixed points, such as

the triple point of hydrogen
the triple point of neon
the triple point of water
the freezing point of zinc
the freezing point of silver
the freezing point of gold
etc.,

are assigned certain values. In the cases of the six points listed, these values are

13.8033
24.5561
273.16
692.677
1234.93
1337.33

kelvin respectively.

A number of standard instruments are to be used in different temperature ranges, with defined interpolation formulas for temperatures between the fixed points. A complete description of ITS90 would be rather lengthy (see, for example, http://www.omega.com/techref/intltemp.html), but its purpose is to reproduce as precisely as practically possible the absolute temperature scale as defined by the Carnot engine.