Thermometry

To define a temperature scale, one begins by choosing a “thermometric property”—that is, some property of matter that depends on the temperature. The length of a thin tube of mercury or colored alcohol is a common example. Others include the resistance of metals (for example, platinum) or semiconductors, the emf produced by a thermocouple, and the pressure of a constant volume gas thermometer. Then, one defines a temperature scale \( t(x) \) through an equation of the form

\[
t(x) = ax + b,
\]

where \( x \) is the thermometric property. Note that this scale is linear by definition. Today, the usual practice is to

- set \( b = 0 \); and
- use some easily determined “fixed point” to determine \( a \).

In this case, if \( t(x_0) \) and \( x_0 \) represent the temperature and value of the thermometric property of the “fixed point”—a temperature that is easy to reproduce—then we have

\[
t(x_0) = ax_0.
\]

At any other temperature,

\[
t(x) = ax
\]

and hence

\[
\frac{t(x)}{t(x_0)} = \frac{x}{x_0} \quad \text{or} \quad t(x) = t(x_0) \frac{x}{x_0}.
\]

The choice of fixed points can depend on the particular temperature regime in which one is most interested. Formerly, freezing or boiling points were commonly used as fixed points. Today, however, the triple point of water is used as the basis for the Kelvin temperature scale. The text by Zemansky and Dittman, *Heat and Thermodynamics*, contains a good discussion, and the earlier editions of this book, by Zemansky, go into even more detail.

Note, of course, that temperature scales defined with different thermometric properties do not necessarily agree with one another. For example, the temperature scale one gets from the resistance of a semiconductor depends exponentially on the Kelvin temperature scale.

In practice, we use the constant volume gas thermometer, using gases and densities that approach the ideal gas law limit. As it happens, this scale agrees well with the one defined by a mercury or alcohol thermometer. More important, this scale also agrees with the much more fundamental temperature scale defined using the Second Law of Thermodynamics!

The next section explains why the triple point is a particularly convenient fixed point.

Phase Diagrams and the Triple Point

Consider an isolated (adiabatic) container of water at 100° C. This container has only water, in vapor and liquid form—no air, or any other substance.
In this container:

- The vapor is in equilibrium with the liquid; that is, if one watches the container, the amounts of vapor and liquid do not change.
- the vapor pressure turns out to be 1 atmosphere (760 mm of Hg).

Suppose that we reduce the temperature to 90° C. Will all of the water vapor suddenly condense to liquid? Obviously not, at least to anyone who has ever been in a steamed-up bathroom or who has experienced a hot July day.

In fact, it turns out that everything is much as it was before, except that the pressure is a little lower, and there is more liquid, and less vapor present. If we do an experiment in which we measure the pressure of the vapor as a function of the temperature, we obtain data similar to those shown below:

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>v.p. (mm Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.6</td>
</tr>
<tr>
<td>20</td>
<td>17.5</td>
</tr>
<tr>
<td>80</td>
<td>355</td>
</tr>
<tr>
<td>100</td>
<td>760</td>
</tr>
<tr>
<td>120</td>
<td>1520</td>
</tr>
</tbody>
</table>

In other words, we find that at any given temperature, the pressure of water vapor in phase equilibrium with liquid water will have some definite, characteristic pressure.

Note also that when the temperature \( T = 100° C \), the vapor pressure is exactly 760 mm Hg—which is just the standard atmospheric pressure (at sea level). It’s not a coincidence—by definition, the normal boiling point of a substance is the temperature at which its vapor pressure is equal to the pressure of 1 atmosphere.

Let’s see if we can make sense of this definition. What characterizes a boiling liquid? [long pause to think deeply!]

Consider a pan of water on a stove—not a closed system, like the one above. Well, when we turn on the heat, eventually it boils—bubbles form. What is inside those bubbles? Not air—we can put pure water, with no dissolved air, in a pan, and it still bubbles away when its temperature reaches the boiling point. So the bubbles must contain water vapor. Why do not bubbles form at lower temperatures? [another long pause to think]

Well, perhaps they start to form; but the atmosphere is exerting a pressure—that is, pushing down—on the surface of the water, with (of course) atmospheric pressure. Suppose the water is at 20° C—its vapor pressure, according to our table, is only 17.5 mm Hg. What would happen to a bubble that tried to form, with the atmosphere pushing down at around 760 mm Hg? Right!
But at 100° C, the vapor pressure of water can sustain itself against the atmosphere—and so bubbles can form!

Questions to ponder:

- Why does water boil at a lower pressure in the mountains, at higher altitudes?
- How does a pressure cooker work?
- Is there anything fundamental about the boiling point of a substance?

We can put this information together in a phase diagram, which is a graph of vapor pressure versus temperature. It will look something like this:

The curve is the line of phase equilibrium between the liquid and vapor phases; thus, \( p_i \) is the vapor pressure at temperature \( T_i \) for a system in which liquid and vapor are in equilibrium in a closed container.

Aside: Note the presence of the critical point—it turns out that the liquid-vapor equilibrium curve does not go on forever, but stops, at a pressure and temperature that is characteristic of a given substance. Here are a few examples:

<table>
<thead>
<tr>
<th>substance</th>
<th>critical temp (K)</th>
<th>critical pressure (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>647.07</td>
<td>22.05</td>
</tr>
<tr>
<td>CO₂</td>
<td>304.14</td>
<td>7.375</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>126.2</td>
<td>3.39</td>
</tr>
</tbody>
</table>

remember that
1 Torr = 1 mm Hg = 133.32 Pa
1 MPa = 10⁶ Pa
temperature conversion: temperature in K = °C + 273.15
1 atmosphere = 0.1013 MPa

data are from Zemansky and Dittman, *Heat and Thermodynamics* (7th ed)
Note that this description of water fits into our everyday experience:

- On a cold day, just above freezing, a small puddle of water evaporates slowly—why?
- On a warm day, the same puddle evaporates much more quickly—again, why?

Let’s think a little more carefully about what goes on when the water in our sealed flask changes temperature. When we reduced the temperature from 100° C to 90° C, we must have done something like the following:

- We place the flask in contact with some object (a pan of water, for example) at a lower temperature.
- Heat flows from the flask to the water in the pan (translation: energy moves from the flask to the water in the pan as a result of a temperature difference).
- In the process, some of the vapor turns into liquid.

It is the last step that interests us here. Apparently the energy lost by the flask comes from the vapor; and as a result of losing that energy, some of the vapor turns into liquid.

We call such a gain or loss of energy, which can take place at constant temperature, a latent heat, or sometimes, a heat of transformation; we will say more about them later on. For now, note that when a pot of water boils, what happens is that the heat from the burner is absorbed by liquid water; as it absorbs the latent heat, the water is transformed into vapor (bubbles), which rise to the top and disperse. This process takes place, of course, at a constant temperature.

So far, we have talked about the vapor and liquid phases. If we consider solids, the phase diagram looks something like this:

There are several points to note here:

- There is a latent heat of vaporization for phase transitions between the liquid and gas phases, and latent heat of fusion for phase transitions between the liquid and solid phases; there is also a latent heat for transitions between the vapor and solid phases.
• For most substances, the slope of the liquid-solid phase equilibrium curve is positive. For water, the slope is negative. It is worth considering the implications of that difference.

We are finally in a position to define the **triple point** — it is just the point at which the two phase equilibrium lines intersect. All substances except helium have triple points. Note that unlike the freezing and boiling points, which depend on external pressure, the triple point is fundamental. When you see a closed container, in equilibrium, that contains solid, liquid, and vapor, you are assured that the substance is at its triple point—a few examples are given in the table. Since triple points are fundamental, they are often convenient for defining temperature scales.

| Triple Points |
|-------------------|-------------------|
| **substance** | **Temp (K)** | **Pressure (kPa)** |
| water | 273.16 | 0.612 |
| CO₂ | 216.6 | 518 |
| nitrogen | 63.15 | 12.46 |

data are from Zemansky and Dittman, *Heat and Thermodynamics* (7th ed); note that the triple point of water is 273.16 K = 0.01° C, slightly above the normal freezing point.

Finally, here are a few other fixed points that are occasionally used.

<table>
<thead>
<tr>
<th>Fixed point</th>
<th>Temperature (K)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triple point of hydrogen</td>
<td>13.8033</td>
<td>-259.3467</td>
</tr>
<tr>
<td>Triple point of oxygen</td>
<td>54.3584</td>
<td>-218.7916</td>
</tr>
<tr>
<td>Normal freezing point of zinc</td>
<td>692.677</td>
<td>419.527</td>
</tr>
<tr>
<td>Normal freezing point of gold</td>
<td>1337.33</td>
<td>1064.18</td>
</tr>
</tbody>
</table>

The data are from Zemansky and Dittman. There is much more to be said along these lines!