**Handout Thermometry**, Temperature, and Thermal Equilibrium

The physician Galen (130 to 200 AD) is the first known to have used the notion of degrees of heat and cold, four degrees each way away from a neutral point. The neutral point was mixed of equal quantities of ice and boiling water. Galen seems to have thought these to be the very hottest and coldest of materials.

There was as yet no instrument to measure the degrees. The ancient Greek Philo's work on pneumatics, which was eventually to lead to thermometry, was lost until Arabic manuscripts were translated. The second edition appeared in 1592, the year in which Galileo took his position in Padua and Galileo is known to have read it by 1594.

The candidates for the honor of having invented the thermometer are Galileo, Santorio, Drebbel, and Fludd. The Italian partisans of Galileo have done their best to magnify his achievements (similar to the British and Newton later on the topic of the Newton Laws).

Their thermometers were based on an air thermoscope, which was in ancient times solely used to entertain by lifting water in a tube by applying heat. Santorio applied first a measuring device to the thermoscope (~ 1612), making it in effect a thermometer. The scale was divided in eight degrees, each divided into minutes.

The Welshman Fludd took a medical degree at Oxford in 1605. He also started from the thermoscope and his letters tell he knew he was making a thermometer. His scale ran from bottom to top in degrees of cold. The exact dates are unclear. Drebbel, a man from the Netherlands, made astronomical clocks for King James of England (1604). It is clear from his letters that Drebbel understood the principle of the thermoscope, and it was used in his clocks to simulate the tides. But the purpose of the instrument was not to be an air thermometer.

The only thing that is clear is that Santorius was the first to use the air thermometer as a scientific instrument.

A major step forward was the use of thermometers with the thermometric fluid sealed in glass. However, the rather peculiar range of properties of glass delayed the development of fixed temperature points and two point scales. For a long time thermometers showed many scales, but the reproducibility was poor nonetheless due to the different properties of the glass other scale developers had been using. By about 1660 the spirit-in-glass thermometer had been developed to satisfactory technical specifications and the mercury thermometer had been temporarily abandoned. One of the few preserved oldest thermometers in the Museo Copernicane in Rome shows 18 temperature scales.

The instrument maker Fahrenheit learned in Denmark from the astronomer Romer, the discoverer of the finite speed of light. Romer left a lab book, which his widow gave in 1739 to the university library in Copenhagen, some 30 years after Romer's death. Meanwhile, his student had continued to add comments to Romer's original observations. It is apparent from the notes that Romer was the first to use the melting point of ice and the boiling point of water as fixed points, and he divided the space in between into equal volume sections, a method very similar to what we use today.

This would be of less interest, if young Fahrenheit had not visited Romer in 1708. Today's temperature scale: setting 32 degrees at the melting point of ice and 212 at the temperature of steam just above pure water boiling (to ensure little fluctuation) at normal atmospheric pressure, the intervals determined by the volumetric expansion of liquid mercury (spirits proved to be expanding non-linearly); closely resembles the last of three temperature scales Fahrenheit developed. In practice, Fahrenheit's second fixed point was not the boiling water temperature but human body temperature (96 degrees).

In France, Fahrenheit's scale remained unused and even unknown. There, Reaumur showed the way, which he documented in surprisingly verbose monographs. He took a long time to document an instability of the boiling point temperature, which was, unbeknownst to him, due to the variability of atmospheric pressure. Reaumur deserves credit for recognizing that the volume expansion of mercury was superior to that of alcohol spirits.

There is little written about the melting point of ice to this point. The French had an edge because some very deep cellars of the university in Paris had rather stable low temperatures, whereas elsewhere it was difficult to have a freezing point reference when it was not winter.

The Swedish astronomer Anders Celsius preferred melting snow over Reaumur's method with the cellar to establish the lower fixed point (the cellar was also not made available to all people, who did work in this field). He made the discovery that water stays at the same temperature until all the snow in it has melted. He also observed that the boiling water depends to some extent on how violently the water boils and that measuring in the steam just above the water is more reliable. Celsius did also begin to use 100 as the degree difference between boiling and freezing. Stromer eventually inverted Celsius' scale and put zero at freezing and 100 at boiling.

Modern Developments

The measurement of temperature is always an indirect measurement. In such experiments, one has to assume a linearity of the phenomenon, which is used for measurement, with temperature. Clearly, when doing this for the very first time we apply circular logic. Fixed points are used to check the deviation from the linear scale, which is engraved on the thermometer, by the progression of the effect in use. Commonly used effects are volume expansion, electric resistivity, magnetic susceptibility, radiant emittance, and thermoelectric effects. All of these come with their own conceptual and model constraints (see lecture discussion).

Six important modern thermometers are the constant-volume gas thermometer, the (platinum) electric resistance thermometer, the thermocouple, saturation helium vapor, paramagnetic salt magnetometry, and blackbody radiation. Each has its own strengths, range of linearity, conceptual weaknesses, and range of application. The constant-volume gas thermometer is considered the most empirical and is treated as a primary thermometer. Its conceptual weakness is the validity of the ideal gas law for dilute gases. Secondary thermometers, like thermocouples and electric resistance thermometers are calibrated on primary thermometers. Primary thermometers are usually unwieldy and impractical. Note that, when compared, different type thermometers give the same reading usually only at one calibration point! It is good practice to use overlapping ranges for thermometers and to change the type of thermometer when one changes into new temperature ranges.

Therefore, the use of reliable fixed points remains crucial. Again we meet a certain degree of circular logic: How did one know in the first place that fixed points are indeed fixed, i.e. always occur the same temperature under comparable conditions? Common fixed points include melting points, vaporization points, superconducting transitions, etc. To ameliorate this conceptual weakness, one always strives for strong theoretical support, which predicts temperature dependences of measuring effects and values of fixed points. This is never straight forward because most of the predictions change with regard to sample purity, pressure, magnetic field, etc.

It is worthwhile to note that thermometers do not measure the temperature of the object they are measuring, but they measure their own temperature. Thus, one has to fall back on the validity of the zeroth law of thermodynamics, in order to have a basis to rely on thermometer readings. One also has to wait long enough for thermal equilibrium to occur between the thermometer and the object whose temperature is in question. Often, one reaches in practice a steady state instead of thermal equilibrium.

Temperature itself is a somewhat elusive and slippery concept without an easily comprehensible meaning: At first one defined it based on the ideal gas law and the zeroth law (see lecture). Later the dependence of entropy on internal energy was used, and one set temperature as the inverse of the slope in that curve. Today, we base our definition of temperature on our knowledge of statistical distributions and take the peak of the Maxwell-Boltzmann speed distribution as our indicator for temperature. Consequently, temperature is undefined when a system is not in thermal equilibrium!