The Zeroth Law of Thermodynamics

At this point we have examined "systems" that are gaseous, liquid and solid from the point of view of developing Equations of State. In and of themselves, these equations of state help us to understand the macroscopic behavior of matter. However, this discussion also provides us with a stepping stone that is placed along the path to understanding the laws of thermodynamics.

And now we do turn to a discussion of the laws of thermodynamics, which will provide a further framework for the study of chemical systems. We will approach these laws using a semi-historical perspective. Not because we are interested in the history of the development of these laws, however interesting it may be, but because this provides us with an easy and conceptual picture of their scope and enunciation. As we do this, we will move pretty far afield from chemistry. We must keep in mind that our discussion will eventually lead us back to theories concerning the physical properties of chemical substances. And these theories will be framed within the framework of thermodynamics. Atkins says this rather grandly:

"Do not think that thermodynamics is only about steam engines: it is about everything. The concepts did indeed emerge during the nineteenth century when steam was the hot topic of the day, but as the laws of thermodynamics became formulated and their ramifications explored it became clear that the subject could touch an enormously wide range of phenomena, from the efficiency of heat engines, heat pumps, and refrigerators, taking in chemistry on the way, and reaching as far as the processes of life."

Peter Atkins
Four Laws that Drive the Universe

Perhaps before moving on, we should re-acquaint ourselves with what it is we mean when we claim some statement is a Law of Nature.

"The observations we make in everyday life as well as the more systematic observations of science reveal certain repetitions or regularities in the world. Day follows night; the seasons repeat themselves in the same order; fire always feels hot; objects fall when we drop them; and so on. The laws of science are nothing more than statements expressing these regularities as precisely as possible."

If a certain regularity is observed at all times and all places, without exception, then the regularity is expressed in the form of a "universal law".

Rudolf Carnap
An Introduction to the Philosophy of Science

But new Laws are not simply passively obtained. They are a result of experimentation. As Carnap continues:
One of the great distinguishing features of modern science, as compared to the science of the earlier periods, is its emphasis on what is called the "experimental method". As we have seen, all empirical knowledge rests finally on observations, but these observations can be obtained in two essentially different ways. In the non-experimental way, we play a passive role. We simply look at the stars or at some flowers, note similarities and differences, and try to discover regularities that can be expressed as laws. In the experimental way, we take an active role. Instead of being onlookers, we do something that will produce better observational results than those we find by merely looking at nature. Instead of waiting until nature provides situations for us to observe, we try to create such situations. In brief, we make experiments.

It is our purpose to examine both the observations and the experiments that have given us the laws of thermodynamics. In this way we will obtain a more complete picture of these Laws.

Now to it.

As usual, Atkins says it best; "thermodynamics is a blunderbuss term originally denoting the study of heat, but is now extended to include the study of the transformations of energy in all its forms. It is based on a few statements that constitute succinct summaries of people's experiences with the way that energy behaves in the course of its transformations. These summaries are the Laws of thermodynamics."

We begin with the Zereth Law of thermodynamics. We begin here because this is where things should logically begin. However, historically, the Zereth Law was the last of the Laws to be formulated; hence its unusual numbering. The Zereth Law establishes that a property called "temperature" exists. Because heat flow is often associated with temperature gradients it is of course important to establish the existence of this property in order to understand heat flow. Because of how it is measured "temperature" was assumed to be a concrete and measureable property, even though this was not the case. So that the thermodynamic framework can be complete, we must consider the Zereth Law and how temperature measurements are made.

Consider a system that is divided into two subsystems; subsystem A and subsystem B. The system is enclosed in a rigid, adiabatic wall. An adiabatic wall separates the two subsystems. Each subsystem is interrogated via some mechanical measurement. For instance, the subsystems might be gases and we might interrogate them by measuring their pressures. The particulars really do not affect the observations of the "regularities" concerning these subsystems.

Now, the adiabatic wall separating the two subsystems is slowly, infinitely slowly, removed and replaced with a rigid, diathermal wall. The pressure gauges, initially reading $P_A$ and $P_B$ begin to readjust themselves and eventually settle on the readings $P_A'$ and $P_B'$. At this point we say subsystems A and B are in Thermal Equilibrium.
We now repeat this procedure using a system constructed of three subsystems; A, B and C. After the adiabatic walls separating the subsystems are replaced with diathermal walls, the pressure readings settle to the values $P_A'$, $P_B'$ and $P_C'$.

![Diagram of subsystems A, B, and C with pressure gauges $P_A'$, $P_B'$, and $P_C'$]

Subsystem A is now in thermal equilibrium with subsystem B. Subsystem B is also in thermal equilibrium with subsystem C.

Now to the EXPERIMENTAL OBSERVATION! If we place subsystem A directly into contact with subsystem C separated by a diathermal wall, the pressure gauges do not readjust themselves.

![Diagram of subsystems A and C with pressure gauges $P_A'$ and $P_C'$]

This tells us that subsystem A and subsystem C were also in thermal equilibrium.

This is always observed to be true. It does not matter what the nature of the systems are or the manner in which they are interrogated. So,

**Zeroth Law of Thermodynamics**

If A is in thermal equilibrium with B, and B is in thermal equilibrium with C, then C will be in thermal equilibrium with A.

This Law was not enunciated until almost ~1930. The observations were considered obvious. However as pointed out above, its statement is needed to complete the thermodynamic framework. As mentioned this is because it establishes that a property we call "temperature" exists. Since the measurement of the temperature of thermodynamic systems is central to establishing the other Laws of thermodynamics, this Law really should have been established first. And, it really was. It was simply not codified until much later.

Now, how do these observations concerning thermal equilibrium establish that a property called "temperature" exists?
The state of each subsystem above is described by the mechanical state variables Pressure ($P$) and Volume ($V$). (The amount of a substance in the subsystem is considered fixed, so the number of moles of material present is not considered a variable.) In this case, thermal contact between A and B ensures that $P_B$ is determined by the state of subsystem B and subsystem A. So, $P_B$ will be a function $g_1$ of $V_B$ and $P_A$ and $V_A$:

$$P_B = g_1(V_B, P_A, V_A)$$

Likewise, thermal contact between subsystem C and subsystem B gives:

$$P_B = g_2(V_B, P_C, V_C)$$

So,

$$g_1(V_B, P_A, V_A) = g_2(V_B, P_C, V_C)$$

By the Zeroth Law, A and C are in thermal equilibrium. So, it should be possible to remove the variable $V_B$ from this equation. Thermal Equilibrium between A and C does not in any way reference subsystem B. This can only be done if we can factor the functions $g$ into the functions $\phi$, $\xi$, and $\eta$ according to:

$$g_1(V_B, P_A, V_A) = \phi_A(P_A, V_A) \xi(V_B) + \eta(V_B)$$

and

$$g_2(V_B, P_C, V_C) = \phi_B(P_C, V_C) \xi(V_B) + \eta(V_B)$$

Then, $g_1 = g_2$ implies:

$$\phi_A(P_A, V_A) = \phi_C(P_C, V_C)$$

Since $\phi(P, V)$ is a completely general function of $P$ and $V$, this last statement can only be true if $\phi(P, V)$ is a constant; denoted by $\tau$:

$$\phi(P, V) = \tau$$

We refer to $\tau$ as the Temperature of the system. The relationship $\tau = \phi(P, V)$ is simply an Equation of State. This should not be surprising. If the subsystems are comprised of Ideal Gases, then the temperature will be denoted by $T$ and the equation of state is:

$$\tau = T = \frac{PV}{nR}$$

If they are composed of van der Waals gases, then:

$$\tau = T = \frac{(p + \frac{\alpha}{V}) (V - b)}{R}$$
Or, if they be liquids or solids:

\[ \tau = t = \left[ \frac{\nu}{\nu_0 (1 - \kappa (P - 1))} \right]^{-1} \]

Now, the Zeroth Law implies that a property called "temperature" exists, but it does not establish how to measure the temperature. This must be done independently using a process called Thermometry.

How do we measure the temperature of a system? There are a number of devices for doing this, each with its own thermometric property. The thermometric property \( y \) responds to different temperatures within a system. The only constraint on the thermometric property is that it must not go through a maximum or a minimum between its operating temperatures \( \tau_{\text{min}} \) and \( \tau_{\text{max}} \).

(Why is this so?)

**Mercury Stick Thermometer**

Thermometric Property = Length of Column of Hg in Stick's Bore

**Constant Volume Gas Thermometer**

Const Volume Gas Cell

Thermometric Property = Pressure of Gas
Thermometric Property = Resistance of Resistor

We establish a Temperature Scale by placing our Thermometer into a low Temperature Bath at temperature $\tau_1$, such as an Ice-Water bath, and allow the thermometer to come into thermal equilibrium with the Bath. The thermometer is marked by noting the measurement $y_1$. The thermometer is then placed into a high Temperature Bath at temperature $\tau_2$, say a Steam-Water bath. Again, the thermometer is "marked" by noting the reading $y_2$. These temperature baths are referred to as "Fixed Points".

Now we impose a linearity on the Scale by stating:

$$\frac{dy}{d\tau} = \frac{y_2 - y_1}{\tau_2 - \tau_1} = \text{constant}$$

Now the thermometer is placed into a system whose temperature is to be measured, allowed to come to thermal equilibrium and the "value" of its thermometric property $y$ is "read".
To determine the numeric value of the temperature $\tau$, we start at the fixed point $y_1$ and integrate to $y$:

$$\int_{y_1}^{y} dy = \int_{\tau_1}^{\tau} \left( \frac{y_2-y_1}{\tau_2-\tau_1} \right) d\tau$$

Carrying out the integration:

$$y - y_1 = \left( \frac{y_2-y_1}{\tau_2-\tau_1} \right) \tau - \left( \frac{y_2-y_1}{\tau_2-\tau_1} \right) \tau_1$$

This can be rearranged to determine the temperature reading:

$$\tau = \left( \frac{y-y_1}{y_2-y_1} \right) (\tau_2 - \tau_1) + \tau_2$$

We are familiar with two empirical temperature scales. Originally, the Fahrenheit Scale, established by Daniel Gabriel Fahrenheit in 1724, used three fixed points; a Brine Sol'n ($0^\circ$F), the Ice Point ($32^\circ$F) and Body Temperature ($96^\circ$F).
The later scale of Anders Celsius, established in 1742, used two fixed points; the Ice Point (100°C) and the Steam Point (0°C). Each was established using a Mercury stick thermometer; the linear expansion of a narrow column of Mercury being the thermometric property.

The Ideal Gas Temperature Scale is established using a single fixed point, the Triple Point of Water set at 273.16 Kelvin, and a constant volume gas thermometer. The degree on this scale is named after William Thomson, otherwise known as Lord Kelvin. (Think about how we get away with using a single fixed point for this temperature scale! Refer back to how we established the Ideal Gas Temperature Scale and what the numeric value of \( \tau_1 \) might be taken as.)
A cautionary note is sounded by Castellan (Physical Chemistry, 3rd Ed.):

This reveals a very real difficulty associated with thermometry. A different scale of temperature is obtained for every different property chosen as the thermometric property. Even with one substance, different scales of temperature will be obtained depending on which property is chosen as the thermometric property. Truly, this is an outrageous turn of events. Imagine the consequences if a similar state of affairs existed in the measurement of length: The size of the centimetre would be different depending on whether the meter stick was made of metal or wood or paper.

Interestingly, "Different empirical scales may not be compatible with each other, except for small regions of temperature overlap. If an alcohol thermometer and a mercury thermometer have same two fixed points, namely the freezing and boiling point of water, their reading will not agree with each other except at the fixed points, as the linear 1:1 relationship of expansion between any two thermometric substances may not be guaranteed." (http://en.wikipedia.org/wiki/Scale_of_temperature) Think back to Problem #4 of Problem Set 1.