12.1 Temperature

We often talk about the temperature but what does it really mean? Normally, we think of the temperature as a measure of the hotness of an object but that can be a purely subjective notion. Our sense of whether an object is hot or cold has more to do with the interchange of heat between our skin and the object than the actual temperature. To understand temperature better, we first should consider what happens when two objects are brought into thermal contact.

When two objects are brought into contact such that energy can be transferred between them without the expenditure of any macroscopic mechanical work, the two objects will eventually come into thermal equilibrium with each other and with themselves. The timescale for this process depends on the physical systems and their current states and can range from $10^{-15}$ secs to $10^{10}$ years.

Temperature is that property that is shared when the two systems come into thermal equilibrium. This shared property does not depend upon the detailed structure or properties of the individual systems. Moreover, if energy does transfer between the two objects, we can state that the object that looses energy must be at a higher temperature.

A formal definition of the temperature can be derived from the zeroth law of thermodynamics (Caratheodory).

**Zeroth law of thermodynamics:** Consider a collection of three distinct objects, A, B and C. If A and B are in thermal equilibrium with each other and B and C are also in thermal equilibrium with each other then A and C are in thermal equilibrium with each other.

12.1.1 Thermometers

Thermometers are tools by which one can measure the temperature of a object (via the zeroth law). Thermometers can be subdivided into two groups, primary and secondary.

Primary or absolute thermometers: the behavior of the physical system of the thermometer can be calculated from first principles and directly linked to the absolute temperature.
cally, such thermometers are difficult to use and are only found at national bureaus of standards and are used in calibrating other thermometers and determining the properties of materials.

Secondary thermometers: although the physical property is easier to measure, it cannot be linked to the absolute temperature by a fundamental calculation. A secondary thermometer must be calibrated either against an absolute thermometer or by using a series of known calibration temperatures.

For example, one could use the boiling and freezing points of water as a calibration points for a secondary thermometer but because the temperature at which water boils (or freezes) depends on the ambient pressure, one would have to control the pressure which can introduce errors. To avoid this problem, one can use that temperature at which the solid, liquid and gas phases of a pure substance coexist at a unique temperature and pressure. Such points are called triple points.

For example, the triple point of water is $T_{\text{triple}} = 0.01 \, ^\circ\text{C}$ or on the absolute temperature scale $T_{\text{triple}} = 273.16 \, K$ where $T[K] = T[^\circ\text{C}] + 273.15 \, K$. The pressure at the triple point is 611.73 pascals. Both the Kelvin and Celsius scale are defined by two fixed points, the triple point of water and absolute zero. The International Temperature Scale of 1990 (ITS-90) uses in addition to the triple point of water, the triple points of hydrogen, neon, oxygen, argon and mercury to establish fixed points of the temperature scale.
Examples of physical properties that are often used in secondary thermometers

- the expansion or contraction of a material - mercury thermometers or bimetallic strips
- the resistance of metals or semiconductors
- the voltage generated when the junctions between two dissimilar metals are held at different temperatures - thermocouples

12.1.2 Ideal and Non-Ideal Gas Laws

A good example of a primary thermometer is the ideal gas. Based on theoretical arguments, the pressure an ideal gas should be proportional to the absolute temperature and inversely proportional to the volume, $PV = N k_B T = n R T$ where $N$ is the number of particles and $k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$ is the Boltzmann constant and $n$ is the number of moles and $R = 8.31 \text{ J K}^{-1} \text{ mole}^{-1}$ is the gas constant.

Unfortunately, real gases are not ideal. An implicit assumption in the derivation of the ideal gas law is that the atoms or molecules of the gas occupy no volume and do not interact with
each other. Consequently, real gases only obey the ideal gas law when the particles are separated by very large distances compared to the interaction range and size of the particles. This corresponds to small densities \( \rho = N / V \) or large molar volumes \( v = V / n \).

As the molar volume of the gas decreases, there will be corrections due to the finite size of the particles. In particular, as the molar volume decreases, the pressure should increase faster than predicted by the ideal gas law because the volume available to the gas is reduced by the finite volume occupied by the particles themselves. Denoting the excluded volume associated with the size of the particles as \( b \), we have that

\[
P = \frac{RT}{v-b}
\]

(12.1)

Note that as the molar volume approaches \( b \), the pressure diverges.

If the particles are attracted to each other, then particles within a thin layer near the surfaces of the container will feel a net force towards the interior of the container due to the presence of the particles in the bulk. Consequently the pressure should be less than predicted by the ideal gas law. To estimate the size of the correction, we note that the force on a single particle will be proportional to the density of the gas. In addition, the number of atoms in the layer will also be proportional to the density. The resulting correction becomes

\[
\delta P = -\frac{a}{v^2}
\]

(12.2)

Combining this with our previous result, a good approximation to the pressure of a non-ideal gas becomes

\[
P = \frac{RT}{v-b} - \frac{a}{v^2}
\]

(12.3)

This is the Van der Waal’s equation of state for a non-ideal gas. It contains two constants which can be chosen to fit the data for different gases.

If we assume that the measured temperature of a non-ideal gas is obtained using the ideal gas law, we can substitute the pressure from the Van der Waal’s equation to obtain an estimate for the error in the measured temperature.
\[ T_{\text{eff}} = \frac{PV}{nR} = \frac{Pv}{R} = \frac{v}{R} \left( \frac{RT}{v-b} - \frac{a}{v^2} \right) = \frac{vT}{v-b} - \frac{a}{Rv} = \frac{T}{1 - \frac{b}{v}} - \frac{a}{Rv} \]

Assuming \( v \) to be large and expanding the first term in a power series in \( \frac{1}{v} \) we obtain

\[ T_{\text{eff}} \approx T \left( 1 + \frac{b}{v} + \ldots \mathcal{O} \left( \frac{1}{v^2} \right) \right) - \frac{a}{Rv} \]

\[ T_{\text{eff}} \approx T + \left( bT - \frac{a}{R} \right) \frac{1}{v} \quad (12.5) \]

Therefore depending on the coefficient \( bT - \frac{a}{R} \) for a particular gas, one can obtain different values for the effective temperature. However, in the limit as \( \frac{1}{v} \to 0 \), the effective temperature will approach the true thermodynamic temperature. There one can use several gases at smaller and smaller molar volumes to extrapolate to the true temperature.

Figure 12.2  The triple point of water measured using three different gases for a range of densities

As one can see from Fig. 12.2, the measured value of the triple point temperature depends on
the type of gas and the molar volume. Taking this into account, one can define the tempera-
ture based on the ideal gas law as

\[
T = 273.16 \lim_{P \to 0} \frac{P}{P_{\text{triple}}}
\]  

(12.6)

12.2 Thermal Properties of Materials

12.2.1 Thermal Expansion

Most materials expand when they are heated. Such behavior can be understood in terms of
the interaction potential between the atoms or molecules in the material. At large distances
the interaction is attractive (material is cohesive) but when the atoms become closer than the
atomic radii, the interaction becomes repulsive (material is incompressible).

Figure 12.3  Effective potential energy between atoms in a material. (Lennard-Jones or 6-12
potential)

At a given temperature, the atoms will have some thermal energy (blue) corresponding to
small oscillations about the minimum of the potential. On average, the separation between
the atoms is indicated by \( < r > \). As the temperature increases, the thermal energy increases
(red) with a corresponding larger amplitude of oscillations. However because the potential is
not harmonic \( V(r) = \frac{1}{2} k x^2 \), the average separation for the atoms shifts to a larger value.

This is the origin of the expansion of most materials. Note: if the potential were truly harmonic, no expansion would be observed.

Figure 12.4 The average separation between atoms of a material increases with increasing temperature.

Expanding the length in a Taylor series in \( T \)

\[
L[T] = L[T_0] + \left( \frac{\partial L}{\partial T} \right)_{T=T_0} (T - T_0) + \mathcal{O}(T - T_0)^2
\]

and so for small changes in the temperature, the change in the length of a material will be proportional to the change in the temperature, \( \Delta T \).

\[
\Delta L \propto \Delta T
\]

(12.8)

Now because the expansion of a given length has contributions from each sub-element, the change in length will also be proportional to the overall length. Consequently

\[
\frac{\Delta L}{L} = \alpha \Delta T
\]

(12.9)
where $\alpha$ is the linear expansion coefficient for a material. Some values taken at room temperature and at liquid nitrogen temperature can be seen in the table.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\alpha (K^{-1}) @ 293 K$</th>
<th>$\alpha (K^{-1}) @ 80 K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>$2.4 \times 10^{-5}$</td>
<td>$7.5 \times 10^{-6}$</td>
</tr>
<tr>
<td>Brass</td>
<td>$2.0 \times 10^{-5}$</td>
<td>$9.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>Copper</td>
<td>$1.7 \times 10^{-5}$</td>
<td>$7.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>$1.5 \times 10^{-5}$</td>
<td>$6.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>Pyrex</td>
<td>$1.8 \times 10^{-6}$</td>
<td>$1.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>&quot;Invar (NiFe alloy)&quot;</td>
<td>$9.0 \times 10^{-7}$</td>
<td>$5.0 \times 10^{-7}$</td>
</tr>
<tr>
<td>Silica</td>
<td>$4.7 \times 10^{-7}$</td>
<td>$5.0 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

Table 12.1 Table of linear expansion coefficients at room temperature and at 80 K.

Example: What is the change in length of a 10 m long rod of aluminum for 10 °C change in the temperature at room temperature?

\[
\Delta L = \alpha L \Delta T \\
= \frac{0.000024}{K} \times 10 m \times 10 K \\
= 0.0024 m = 2.4 mm
\]

12.2.2 Thermal Stress

Even for small changes in temperature, there can be fairly large induced stress in the material. For a steel rod, $\alpha = 1.5 \times 10^{-5}$ $K^{-1}$, the relative change in length becomes

\[
\frac{\Delta L}{L} = (1.5 \times 10^{-5} K^{-1}) \Delta T
\]

(12.11)

If the steel rod is fixed to a rigid structure, how much force is required to keep the length constant? The force is given by Young’s modulus

\[
F = Y A \frac{\Delta L}{L} \quad \text{where for steel } Y = 20 \times 10^{10} N m^{-2}
\]

(12.12)
Assuming that the cross sectional area of the rod is \( A = 1 \text{ cm}^2 = 1 \times 10^{-4} \text{ m}^2 \), the pressure, \( P = \frac{F}{A} \), required to keep the length constant becomes

\[
P = \frac{F}{A} = \frac{Y \Delta L}{L} = 2. \times 10^{11} \frac{N}{m^2} \times 1.5 \times 10^{-5}
\]

\[
\frac{1}{K} \Delta T = 3. \times 10^6 \Delta T \frac{N}{K m^2} = 435. \Delta T \frac{PSI}{K}
\]

So for a change of a few degrees in temperature, one requires hundreds of PSI’s to keep the length of the rod constant. If the temperature change is negative, this force can be sufficient to break the rod or if the temperature change is positive, the rod could buckle.

12.2.3 Buckling

Even though this appears to be an insignificant change in the overall length, it can produce some dramatic effects such as buckling (http://www.halcrow.com/Areas-of-expertise/Climate-change-adaptation/) and seizing of mechanical parts.

To see how this is possible, consider the same length rod of aluminum undergoing a 10 °C change in temperature. If the ends of the rod are fixed, how much does the rod have to bow
to accommodate the thermal expansion? Assuming that the rod assumes the shape of an arc of a circle of radius $R$, the arc length is $s = 2R\phi$ and the cord length is $s_0 = 2R\sin(\phi)$ and the deviation from the cord at the center of the arc is $\delta = R - R\cos\left(\frac{\phi}{2}\right) = R\left(1 - \cos\left(\frac{\phi}{2}\right)\right)$.

\[ S = R\phi \]
\[ s_0 = 2R\sin\left(\frac{\phi}{2}\right) \]

Then the ratio of the change in length of the rod to the initial length becomes

\[ \frac{s - s_0}{s_0} = \left(\frac{R\phi - 2R\sin\left(\frac{\phi}{2}\right)}{2R\sin\left(\frac{\phi}{2}\right)}\right) = \frac{\phi - 2\sin\left(\frac{\phi}{2}\right)}{2\sin\left(\frac{\phi}{2}\right)} \quad (12.14) \]

Because the change in length is small, we would expect the angle should also be small. Expanding the $\sin\left(\frac{\phi}{2}\right)$ in a Taylor’s series, $\sin[x] \approx x - \frac{x^3}{6} + O[\phi^6]$ so that $2\sin\left[\frac{\phi}{2}\right] \approx \phi - \frac{\phi^3}{24} + O[\phi^6]$ and so

\[ \frac{s - s_0}{s_0} \approx \frac{\phi^2}{24} + O[\phi]^4 \quad (12.15) \]

Given that the relative change in length is just $\frac{\Delta L}{L} = \alpha \Delta T = \frac{\phi^2}{24}$, we can solve for $\phi = \sqrt{24 \alpha \Delta T}$ . The radius $R$ can be found from the original length, $R = \frac{L}{\sin[\phi/2]}$. Substituting this into our expression for $\delta = R\left(1 - \cos\left[\frac{\phi}{2}\right]\right)$ and again expanding for small $\phi$
\[ \delta = R \left( 1 - \cos \left( \frac{\phi}{2} \right) \right) = \frac{L \left( 1 - \cos \left( \frac{\phi}{2} \right) \right)}{2 \sin \left( \frac{\phi}{2} \right)} = \frac{L \phi}{8} + \frac{L \phi^3}{384} + O[\phi]^4 \]

and so to lowest order the deviation becomes

\[ \delta \approx \frac{L \phi}{8} \approx \frac{1}{2} \sqrt[3]{\frac{3}{2}} L \sqrt{\alpha \Delta T} \quad (12.17) \]

Substituting in the numbers for the 10 m long aluminum rod for a 10 K change in temperature, one obtains

\[ \delta \approx 0.0948683 \text{ m} \quad (12.18) \]

One can also use differential thermal expansion to one’s advantage. For example by binding two materials with different thermal expansion coefficients (bimetallic strip), one can generate motion as a function of temperature.
12.2.4 Volume Expansion

For a 3 dimensional object, the expansion coefficient will in general anisotropic, i.e. the value of the coefficient will be different in different directions of the material. Writing the volume of the object as $V = L_1 L_2 L_3$, then each length will expand according to the expansion coefficient appropriate for that direction.

The expanded volume to first order in the change is given by

$$V^* = (L_1)^* (L_2)^* (L_3)^* = (L_1 + \Delta L_1) (L_2 + \Delta L_2) (L_3 + \Delta L_3)$$

$$\approx L_1 L_2 L_3 + L_2 L_3 \Delta L_1 + L_1 L_3 \Delta L_2 + L_1 L_2 \Delta L_3$$

$$\approx L_1 L_2 L_3 \left( 1 + \frac{\Delta L_1}{L_1} + \frac{\Delta L_2}{L_2} + \frac{\Delta L_3}{L_3} \right)$$

(12.19)
Therefore the relative change in the volume becomes

\[
\frac{\Delta V}{V} = \frac{-V + V'}{V} = \frac{L_1 L_2 L_3 (1 + \Delta T \alpha_1 + \Delta T \alpha_2 + \Delta T \alpha_3) - L_1 L_2 L_3}{L_1 L_2 L_3} = \Delta T (\alpha_1 + \alpha_2 + \alpha_3)
\]

(12.20)

Depending on the structure of a crystal, all of the \( \alpha \)'s can be different. In fact, for some materials, some of the \( \alpha \)'s can be negative. For isotropic systems, all directions are equivalent and the relative change in the volume is simply

\[
\frac{\Delta V}{V} = 3 \alpha \Delta T = \beta \Delta T
\]

(12.21)

where \( \beta \) is the coefficient of volume expansion.

---

**Table 17.2** Coefficients of Volume Expansion

<table>
<thead>
<tr>
<th>Solids</th>
<th>( \beta ) [K (^{-1}) or (C(^\circ)) (^{-1})]</th>
<th>Liquids</th>
<th>( \beta ) [K (^{-1}) or (C(^\circ)) (^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>( 7.2 \times 10^{-5} )</td>
<td>Ethanol</td>
<td>( 75 \times 10^{-5} )</td>
</tr>
<tr>
<td>Brass</td>
<td>( 6.0 \times 10^{-5} )</td>
<td>Carbon disulfide</td>
<td>( 115 \times 10^{-5} )</td>
</tr>
<tr>
<td>Copper</td>
<td>( 5.1 \times 10^{-5} )</td>
<td>Glycerin</td>
<td>( 49 \times 10^{-5} )</td>
</tr>
<tr>
<td>Glass</td>
<td>( 1.7 \times 10^{-5} )</td>
<td>Mercury</td>
<td>( 18 \times 10^{-5} )</td>
</tr>
<tr>
<td>Invar</td>
<td>( 0.27 \times 10^{-5} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz (fused)</td>
<td>( 0.12 \times 10^{-5} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steel</td>
<td>( 3.6 \times 10^{-5} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 12.2 Table of volume expansion coefficients

Defining the density as \( \rho = \frac{N}{V} \), then the change in the density becomes

\[
\Delta \rho = \frac{N \Delta}{V} = - \frac{N \Delta V}{V^2} = - \frac{\Delta V \rho}{V}
\]

(12.22)

and so
Now there are many materials which exhibit interesting behavior. One of best known is the density of water as a function of temperature. With decreasing temperature, water becomes more dense (contracts) down to 4 °C. Below this temperature, water expands with decreasing temperature. Water is also anomalous in that ice is less dense than the liquid (as seen from the figure).

\[ \frac{\Delta \rho}{\rho} = -\frac{\Delta V}{V} = -\beta \Delta T \]  

(12.23)

Another unusual material is rubber which also contracts upon heating. As we shall see later, this has to do with the fact that rubber is made from long chain molecules.

12.2.5 Mechanical Equivalent of Heat

In the 1700’s, it was not understood that heat is in fact energy. It was believed to be a real substance that flows from a hotter object to a colder object. The first evidence that heat could not be a substance was given by Benjamin Thompson (1753-1814), an American from Woburn, Massachusetts. He was a loyalist and had to flee to England during the American Revolutionary war. He later moved to Bavaria and because of his government service was named Count Rumford. In 1798, he noticed that when boring a cannon, the resulting chips are hot. This made perfect sense according to the prevalent theory of phlogiston. In this
theory, the ability of a material to hold the heat substance or phlogiston was diminish when the material is subdivided. For this reason, when wood becomes ash, it releases heat. Count Rumford noticed however that if the boring tool was dull and did not generate any chips, the constant rubbing of the boring head in the cannon produced a constant flow of heat.

A formal experiment that links mechanical energy and heat was made by James Joule (1818-1889). He was the son of a brew master. At that time, brew master had very accurate and sensitive thermometers. In his apparatus, a liquid was stirred by a mass falling a given distance. The motion of the liquid eventually dissipates due to friction and resulted in a change in the temperature of the liquid. In 1843, Joule showed that this change in temperature was proportional to the potential energy lost by the falling mass (772.24 foot pound force for a change of 1°F in 1 pound of water).

![Figure 12.7 Engraving of Joule's apparatus for measuring the mechanical equivalent of heat. Source: Harper's New Monthly Magazine, No. 231, August, 1869.](http://en.wikipedia.org/wiki/File:Joule%27s_Apparatus_(Harper%27s_Scan).png)

The current conversion is that the energy required to raise the temperature of 1 gram of water by 1°C is 1 calorie or 4.186 Joules. (Note: the Calorie used in food science to denote chemical energy is actually 1 kilocalorie).

### 12.2.6 Heat Capacity

The expression heat capacity comes from the old theory of phlogiston in which a material had an ability to hold heat. It is properly defined as the coefficient that relates the amount of heat
required to change the temperature of an object. For an object the total heat capacity, $C$, is
given by

\[ Q = C \Delta T \]  

(12.24)

This heat capacity is extensive because it scales with the size of the system. One can also
define intensive coefficients, the specific heat capacities, that do not scale with the size of the
system. For example, one can normalize the total heat capacities by the mass of the system,
the number of particles or the number of moles in the system.

\[ c_m = \frac{Q}{m \Delta T} \]  

(12.25)

\[ c_N = \frac{Q}{N \Delta T} \]

Table 12.3 Table of specific heats and molar heat capacities

<table>
<thead>
<tr>
<th>Substance</th>
<th>Specific Heat, $c$ (J/kg·K)</th>
<th>Molar Mass, $M$ (kg/mol)</th>
<th>Molar Heat Capacity, $C$ (J/mol·K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>910</td>
<td>0.0270</td>
<td>24.6</td>
</tr>
<tr>
<td>Beryllium</td>
<td>1970</td>
<td>0.00901</td>
<td>17.7</td>
</tr>
<tr>
<td>Copper</td>
<td>390</td>
<td>0.0635</td>
<td>24.8</td>
</tr>
<tr>
<td>Ethanol</td>
<td>2478</td>
<td>0.0461</td>
<td>111.0</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>2380</td>
<td>0.0820</td>
<td>148.0</td>
</tr>
<tr>
<td>Ice (near 0°C)</td>
<td>2100</td>
<td>0.0180</td>
<td>37.8</td>
</tr>
<tr>
<td>Iron</td>
<td>4.11</td>
<td>0.02399</td>
<td>26.5</td>
</tr>
<tr>
<td>Lead</td>
<td>130</td>
<td>0.207</td>
<td>26.9</td>
</tr>
<tr>
<td>Marble (CaCO$_3$)</td>
<td>870</td>
<td>0.100</td>
<td>87.9</td>
</tr>
<tr>
<td>Mercury</td>
<td>138</td>
<td>0.201</td>
<td>27.7</td>
</tr>
<tr>
<td>Salt (NaCl)</td>
<td>879</td>
<td>0.0585</td>
<td>51.4</td>
</tr>
<tr>
<td>Silver</td>
<td>234</td>
<td>0.108</td>
<td>25.3</td>
</tr>
<tr>
<td>Water (Liquid)</td>
<td>4190</td>
<td>0.0180</td>
<td>75.4</td>
</tr>
</tbody>
</table>

Table 12.3  Table of specific heats and molar heat capacities

As one can see from the table of heat capacities, the heat capacity of water (either per kilogram
or per mole is fairly large compared to those of metals. Such a large heat capacity has a
profound moderating effect on the weather.
The temperature dependence of the specific heat can lead to many physical insights into the behavior of the materials.

For example, the specific heat of an insulating crystalline solid was believe to be a constant independent of the temperature with the Dulong-Petit value of $3R$. However, low temperature measurements showed that the specific heat decreased with decreasing temperature and that different materials showed different characteristic temperatures at which the specific heat deviated from the Dulong-Petit value. The characteristic temperature for diamond is one of the highest known.

![Graph showing specific heat vs temperature for Germanium and Diamond](image)

**Figure 12.8** The specific heats of Germanium and Diamond as a function of temperature. Note that diamond deviates from the Dulong-Petit value at a much higher temperature.

The behavior of the specific heat near phase transitions can help to identify the type or “order” of the phase transition.
12.2.7 First Order Phase Transitions

A first order phase transition is characterized by the coexistence of two distinct phases. For example, as can be seen in Figure 12.8, at a pressure of 1 atm, the solid and liquid phases coexist at a temperature of 273 K (the point SL). In fact the entire line represents the range of temperature and pressure at which solid and liquid can coexist. Similarly there are coexistence lines for solid and gas as well as for liquid and gas. The liquid-gas coexistence curve has the unique properties that it terminates at the point E. Beyond this point there is no distinction between a gas and liquid. In fact, it is possible to take a sample of water from a point deep within the liquid phase go around the critical point to a point deep within the gas phase without ever seeing a meniscus.

Figure 12.10 Phase diagram of water indicating the solid-liquid, solid-gas and liquid-gas coexistence curves.

In order to convert a given amount of one phase into another, a certain amount of heat energy must be transferred which is called the heat of transformation or the latent heat.
For example, as one adds heat to ice at 1 atm, the temperature of the ice will increase according to the heat capacity of ice along the dashed line until it reaches the coexistence curve. At this point, the temperature will remain fixed even though heat is still being added until all of the ice is melted and converted into water. At that point, the temperature will again start to rise according to the heat capacity of water.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Normal Melting Point</th>
<th>Heat of Fusion, $L_f$ (J/kg)</th>
<th>Normal Boiling Point</th>
<th>Heat of Vaporization, $L_v$ (J/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium</td>
<td>°</td>
<td>4.216, $-269.90$</td>
<td>405.4</td>
<td>$20.9 \times 10^3$</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>°</td>
<td>58.6, $10^3$</td>
<td>20.26</td>
<td>$552 \times 10^3$</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>°</td>
<td>77.94, $10^3$</td>
<td>21.3</td>
<td>$703 \times 10^3$</td>
</tr>
<tr>
<td>Oxygen</td>
<td>°</td>
<td>90.15, $10^3$</td>
<td>21.3</td>
<td>$213 \times 10^3$</td>
</tr>
<tr>
<td>Ethanol</td>
<td>°</td>
<td>104.2, $10^3$</td>
<td>51</td>
<td>$854 \times 10^3$</td>
</tr>
<tr>
<td>Mercury</td>
<td>°</td>
<td>650.8, $10^3$</td>
<td>272.8</td>
<td>$272 \times 10^3$</td>
</tr>
<tr>
<td>Water</td>
<td>°</td>
<td>334, $10^3$</td>
<td>100</td>
<td>$226 \times 10^3$</td>
</tr>
<tr>
<td>Sulfur</td>
<td>°</td>
<td>213, $10^3$</td>
<td>526</td>
<td>$226 \times 10^3$</td>
</tr>
<tr>
<td>Lead</td>
<td>°</td>
<td>254, $10^3$</td>
<td>871</td>
<td>$526 \times 10^3$</td>
</tr>
<tr>
<td>Antimony</td>
<td>°</td>
<td>165, $10^3$</td>
<td>551</td>
<td>$871 \times 10^3$</td>
</tr>
<tr>
<td>Silver</td>
<td>°</td>
<td>2406, $10^3$</td>
<td>2536</td>
<td>$551 \times 10^3$</td>
</tr>
<tr>
<td>Oxd</td>
<td>°</td>
<td>2933, $10^3$</td>
<td>1278</td>
<td>$2536 \times 10^3$</td>
</tr>
<tr>
<td>Copper</td>
<td>°</td>
<td>1460, $10^3$</td>
<td>5069</td>
<td>$1278 \times 10^3$</td>
</tr>
</tbody>
</table>

* A pressure in excess of 25 atmospheres is required to make helium solidify. At 1 atmospheric pressure, helium remains a liquid down to absolute zero.

Figure 12.11 Temperature of water as a function of time for a constant influx of heat, $\dot{Q} = 1000$ Watts
12.2.8 Thermal Conduction

Heat is transported across an object under an imposed thermal gradient, \( T_2 > T_1 \).

Where the rate at which heat is transported is given by \( \dot{Q} = \frac{\Delta Q}{\Delta t} \) or \( \frac{dQ}{dt} \). For a small temperature difference, the flow of heat through an object will be proportional to the change in temperature, \( \dot{Q} \propto (T_2 - T_1) = \Delta T \). If two objects of the same material and shape are placed in series and the temperature difference across each object is the same then the flow of heat in each object will be the same.

The total flow of heat through the combined object will be proportional to the total change in the temperature divided by the total length,

\[
\dot{Q} \propto \frac{(T_2 - T_1)}{\Delta L} = \frac{(T_3 - T_2)}{\Delta L} = \frac{(T_3 - T_1)}{2 \Delta L} = \frac{\Delta T_{\text{total}}}{\Delta L_{\text{total}}}.
\]

Similarly putting these two objects in parallel, it is clear that the total flow of heat will be doubled or equivalently proportional to the area of the combined object, \( \dot{Q} \propto \frac{\Delta T}{\Delta L} \frac{A}{2} = \frac{\Delta T_{\text{total}}}{\Delta L_{\text{total}}} \frac{A_{\text{total}}}{2} \).

The proportionality constant is called the conductivity of the material and will be an intrinsic property of the material, \( \dot{Q} = \kappa \frac{\Delta T}{\Delta L} A \) where the dimensions of \( \kappa \) are \( \text{Joule/sec/mK} \). Taking the limit as the change in length becomes small, we obtain the differential form,
\[
\dot{Q} = \frac{dQ}{dt} = -\kappa A \frac{dT}{dx} = -\kappa A \nabla T
\]  

(12.26)

where the minus sign indicates that heat flow from hot to cold. Defining a heat flux

\[
\mathbf{J}_Q = \frac{\dot{Q}}{A} = -\kappa \nabla T
\]  

(12.27)

This equation is very similar to the relationship between the current flowing through a resistive object under the action of an electric field

\[
I = \frac{dq}{dt} = \frac{V}{R} = \frac{\Delta L \mathcal{E}}{R} = -\frac{\Delta L}{R} \nabla \Phi
\]  

(12.28)

Because the current will be proportional to the area of the wire, we can define a current density, \( J_e = I / A \) and

\[
J_e = -\frac{\Delta L}{RA} \nabla \Phi = -\sigma \nabla \Phi
\]  

(12.29)

where \( \sigma = \frac{\Delta L}{RA} \) is the electrical conductivity which is the inverse of the electrical resistivity, \( \rho = \frac{1}{\sigma} = R \frac{A}{\Delta L} \) or \( R = \rho \frac{\Delta L}{A} \).

Typically good metals that have large electrical conductivities also have large thermal conductivities because both depend upon the free motion of the electrons within the metal. The fact that it is the electrons that transports the heat through the system leads to more interesting behavior. Applying a thermal gradient can give rise to a voltage difference (Seebeck effect). An electrical current can give rise to a thermal gradient (Peltier effect).

Most insulators are poor conductors of heat. In these systems the transport of heat is through the vibrations of the lattice (phonons).
12.2.9 Convection

In convection, the heat is transported through the system by the motion of a fluid (gas or liquid). The fluid is heated at the hot end by conduction and then the heat is carried by the fluid to the cold end where it is cooled by conduction. The flow can either be forced by an external fan or pump or driven by an instability induced differences in the density of the fluid due to thermal expansion. When driven by differences in density, the fluid sets up convection cells in which the fluid in a given section of the system forms closed circulating loops. Such convection cells can be seen in a pot of water on the stove, regions on the surface of the sun and upwelling and subduction of the mantle of the earth. Convection is a very non-linear process and is therefore difficult to model.

12.2.10 Radiation
Another way in which heat can be transferred from a hot object to a colder object is by the emission and absorption of radiation in the form of electromagnetic waves. All objects radiate according to their temperature over a range in frequencies or wavelengths. Consider an empty box heated to a temperature $T$. Within the box, there will be thermal radiation within the box. The presence of this radiation can be observed by opening a small hole in the walls of the box. For example, you know that the interior of a very hot oven will glow red. In addition, you can feel the heat radiated from the hole in the box. Planck showed that the density of energy per unit wavelength within the box is given by

$$U_\lambda(\lambda) d\lambda = \frac{8 \pi h c}{\lambda^5} \frac{1}{e^{h c/\lambda k_B T} - 1} d\lambda$$

(12.30)

where $U_\lambda(\lambda) d\lambda$ is the energy per unit volume whose wavelength is between $\lambda$ and $\lambda + d\lambda$.

*Figure 12.12  The Planck distribution for the blackbody radiation radiated by objects at three different temperatures*

For an object at room temperature, most of the radiation is in the infrared ($1 - 100 \mu m$). As the temperature of the object increases, the wavelength of the radiation becomes shorter. The characteristic color of a hot object like a star is directly related to shape of the distribution curve for blackbody radiation.
The peak in the distribution is given by the Wien displacement law,

\[ \lambda_{\text{peak}} T = 2.898 \times 10^{-3} \text{ m K} \] (12.31)

After the big bang, the universe expanded and cooled. At the present time, the ambient temperature of the blackbody radiation from the big bang is approximately 3 K. At this temperature, the peak in the radiation is in the microwaves, \( \lambda_{\text{peak}} = 0.966 \text{ mm} \).
Figure 12.13  Planck distribution for a blackbody at 3 K

The COBE and WMAP satellites have been used to study the anisotropy of the blackbody radiation in universe.

Figure 12.14  The Cosmic Microwave Background temperature fluctuations from COBE and WMAP

If one integrates over the Planck distribution, one can obtain the total power radiated per unit area $|\mathcal{S}|$ (energy flux) by an object at a temperature, $T$. This energy flux is given by the Stefan-Boltzmann law

$$|\mathcal{S}| = \sigma \varepsilon T^4$$  \hspace{1cm} (12.32)

where $\sigma = 5.6696 \times 10^{-8} \frac{W}{m^2 K^4}$, is the Stefan-Boltzmann constant and $\varepsilon$ the emissivity is a material constant that measures the ability of the material to emit energy by radiation. A true black body has an emissivity of one, $\varepsilon = 1$. 
As an object radiates energy, it will also absorb radiation from its surroundings. If the surroundings have a uniform temperature, $T_0$, the net power transferred from the object to the surroundings is given by

$$\text{Power} = A \frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2 - \epsilon_1 \epsilon_2} \left( T^4 - T_0^4 \right)$$  \hspace{1cm} (12.33)$$

where $A$ is the area of the object and $\epsilon_1$ and $\epsilon_2$ are the emissivities of the object and surroundings.