Thermodynamics
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Thermodynamics links the variables describing the state of matter at the macroscale (such as temperature, pressure, volume and density) with which we are familiar with the submicroscale behavior of matter (individual atoms and molecules moving and colliding with random motion).

Temperature, Heat, and Internal Energy

What is temperature? What is heat? What is internal energy? You probably know the three are related but they are definitely not the same thing. We will work our way through to understand each of these and how they relate to one another.

Temperature

A simple definition of **temperature** is that it is a property of matter that you measure with a thermometer. This is a ***macroscopic*** definition that links it to a measurement. We will also quantitatively link temperature to the ***submicroscopic*** behavior of molecules and find that temperature is proportional to the kinetic energy of the molecules.

Thermometers measure a property of matter that changes as the matter gets hotter or colder. Metals, liquids and gases expand as they get hotter. Differential expansion of two metal strips attached to one another causes the strip to coil and was a method used commonly in thermostats. When very hot, most substances emit radiation which can be measured and used to determine an object's temperature remotely. Certain marked changes like the phase changes of freezing/melting and boiling/condensation occur at very specific temperatures. Phase changes such as these have been proposed for blackbody calibration sources for climate monitoring radiometric sensors on future spacecraft that are purported to provide international standard (SI) traceability of calibration in orbit.

Consider a constant volume gas thermometer which is a very simple device. Its behavior is characterized by the simple relation:

$$T = a\,P$$

where T is temperature and P is pressure. So temperature is proportional to pressure when the volume and number density of the gas are fixed. There is also a proportionality constant, a, that we need to understand.

IDEAL GAS CONCEPT

The equation above indicates there is an *absolute* temperature if the gas behaves as an *ideal* gas. At the molecular level, an ideal gas is one where

1. the size of the molecules is negligible compared to the average separation between molecules and
2. the average potential energy of interaction between two molecules is negligible compared to their average kinetic energy.

The collisions between ideal gas molecules are equivalent to perfectly elastic collisions between billiard balls.

Macroscopically, the constant, a, in the equation above depends on density.

At "normal" densities, most gases such as hydrogen, helium, nitrogen and oxygen, behave very nearly as ideal gases. Water vapor behaves less ideally because the water vapor molecules "feel" one another at greater distances and may stick to one another in a collision, behavior that is associated with their very large permanent electric dipole moment and binding energy. Accounting for this effect requires small correction factors relative to ideal behavior.

The SI unit of temperature is the Kelvin which is defined as setting the temperature at the triple point of water equal to 273.16 K.

At normal pressure, water freezes at one temperature ($0^oC = 32^oF$) and boils at another temperature ($100^oC = 212^oF$). The boiling point occurs when the saturation vapor pressure of water vapor equals the air pressure. Reducing the air pressure reduces the boiling point of water. (This is why pressure cookers are required at high altitude to cook food). When the air pressure is reduced to ~6 millibars, water freezing point and boiling point are equal. At this condition, called the triple point, solid, liquid and gas phases of water exist in equilibrium. The reproduciblity and uniqueness of this triple point allow it to be used to calibrate the Kelvin scale. The strange number of 273.16K is chosen to create a scale that is simply an offset from the existing Celsius scale where the freezing point of water is 0^oC and the boiling point under normal atmospheric conditions is 100^oC.

So we can combine this triple point knowledge with the equation above to determine a value for the constant, *a*, in the equation above such that

$$T = \left(\frac{273.16}{P_{triple}}\right)P$$

So this thermometer can measure absolute temperature and actually be used to define absolute temperature so long as the gas behavior remains ideal. Eventually at low enough temperatures, the gas density will increase such that the behavior will no longer be ideal. In fact the gas will likely condense to a liquid or solid at some point.

Another point that I used to make in my measurements class about thermometers is the temperature that they measure is the temperature of the thermometer. It is very important that the thermometer be in equilibrium with the medium whose temperature it is measuring or else its temperature will not be that of the medium.

Temperature Scales

Celsius scale: $T(^oC) = T(K) - 273.15$

Fahrenheit scale: $T(^oF) = T(^oC)\ 9/5 + 32$

Rankine scale: $T(^oR) = T(K)\ 9/5$

The Mole

An atom is defined in the periodic table of elements by the number of protons in its nucleus. The number of neutrons in a given atoms can vary although one particular number of neutrons is typically be far the most common for a given atom. Atoms with different numbers of neutrons are called isotopes.

The most common atom of carbon found in nature contains 6 protons and 6 neutrons and is designated as ^{12}C. It represents about 99% of the naturally occurring carbon. ^{13}C represents the other 1%. The atomic mass unit (amu) is defined such that an atom of ^{12}C has a mass exactly equal to 12 amu. On this scale, the lightest isotope of hydrogen, ^{1}H, has a mass of 1.0078 amu.

$$1 \text{ amu} = 1.6605 \times 10^{-24} \text{ gm} = 1.6605 \times 10^{-27} \text{ kg}$$

One mole is the number of atoms whose mass is the same in grams as one atom's mass is in amu. This number is $1/(1.6605 \times 10^{-24})$ and is designated as Avogadro's number, N_0 or N_A.

$$N_A = 6.0222 \times 10^{23} \text{ molecules/mole or amu/gm}$$

Law of Equilibrium, the zeroth law of thermodynamics

When two objects of different temperatures are brought into contact with one another, their two temperatures will adjust toward one another until they both have the same temperature. When they achieve the same temperature, they are said to be in equilibrium. This behavior turns out to be associated with the microscopic theory of temperature and probability of molecular motion.

The ideal gas law

A series of laws were discovered experimentally that led to the ideal gas law.
In 1660 Boyle discovered Boyle's law:

$$PV = \text{constant} \quad (\text{at constant T})$$

In the late eighteenth century, Jacques Charles discovered Charles' law:

$$V = \text{constant} \times T \quad (\text{at constant P})$$

The law associated with the gas thermometer which was first used in 1702 by Guillaume Amontons is

$$P = \text{constant} \times T \quad (\text{at constant V})$$

These gas laws apply to many gases making it apparent that these laws are universal. Combining these laws yields the ideal gas law

$$P\,V = n_V R\,T$$

where P is pressure, V is volume, n_V is the number of moles of the gas in the volume, T is absolute temperature and R is the gas constant whose measured value is 8.314472 J/mole/K. I have previously written the ideal gas law as

$$P = n\,R^*\,T \tag{3}$$

where n is the molar number density of molecules in number of moles per unit volume. n in this equation is equal to n/V in the previous equation. R^* in this equation is equal to R in the previous equation because atmospheric scientists use R to mean $R_{\text{dry}} = R^*/m_{dry}$ where m_{dry} is the mean molecular mass of dry air = 28.96 g/mole. The microscopic version is

$$P = N\,k_B\,T \tag{2}$$

where N is the number density of the gas in units of molecules per unit volume, k_B is Bolzmann's constant: $1.3806503 \times 10^{-23}$ in joules/K and T is the temperature of the gas in Kelvin and

$$R^* = k_B N_A$$