14. The Laws of Thermodynamics

Introduction and Summary

Historically the field of Thermodynamics developed out of a desire to understand the operation of the steam engine so improvements could be made in its efficiency. There are three laws of thermodynamics plus the 0th Law of Thermodynamics which involves the concept of temperature as an indicator of the direction of heat flow. The 1st Law of Thermodynamics is basically a statement of Conservation of Energy applied to thermodynamic systems and it involves the concepts of heat and work as parts of the internal energy of a system. Heat and temperature are different but related concepts that are often confused. Heat is a form of energy (temperature is not) as is work. Work is the energy exchanged with the environment when a parameter like the volume of the system changes. The 2nd Law of Thermodynamics involves a statement of which kinds of processes are allowed by nature (and conversely, the processes that are NOT allowed). In particular, one formulation of the 2nd Law is that it is not possible for heat to flow from a colder object to a warmer object and who would argue with that? However, it can be shown this is equiavlent to the statement that it is impossible to convert a quantity of heat entirely into work! A generalized form of the 2nd Law uses the concept of Entropy and says that all naturally occuring processes have a change in Entropy equal to or greater than zero. Finally the 3rd Law is another statement of something that is not possible. It is not possible to reach the Absolute Zero of Temperature.

Temperature of an Object

The temperature of an object is a familiar concept. You know of various temperature scales: Fahrenheit, Centigrade (Celsius which is slightly different), and the Kelvin or Absolute Temperature Scale. Basically temperature is measured in a way similar to the meter and the kilogram in the sense that there is a standard agreed to by everyone. The meter is an arbitrary distance between two marks on a metal bar and this standard is agreed to by everyone and then the distance between the two marks is divided into an equal number subdivisions (centimeters). Similarly, the two marks of temperature are taken as the freezing and boiling points of water (at one atmosphere pressure). For the Centigrade scale the freezing point is taken as 0°C and the boiling point is taken as 100°C, with 100 degrees in between. The Fahrenheit scale takes the freezing point of water as 32°F and the boiling point of water as 212°F with (212-32)=180°F in between. It is easy to convert from Centigrade to Fahrenheit and the reverse. First you should observe the size of a Fahrenheit degree is different from the size of a Centigrade degree by the ratio of the number of degrees between the freezing point and the boiling point, that is, $(\Delta F/\Delta C)=180/100=9/5$. (The Fahrenheit degrees are smaller because there are more of them.) So there must be a linear relation between the Fahrenheit temperature F and the Centigrade temperature C so you can assume F = (9/5)C + constant, which is the equation of a straight line. The constant is determined by the fact that when C = 0, F = 32 and then the straight-line equation is 32 = (9/5)×0 + constant. Therefore, the constant = 32 and the conversion equation is

$$F = (9/5)C + 32$$

(You could also have gotten the constant by using F=212 when C=100.) The inverse relation is

$$C = (5/9)\times(F - 32)$$

Exercise: Derive this result.

The Kelvin Scale or Absolute Temperature Scale is a little more elegant in that one point is again the freezing point of water but the other point is the temperature where motion ceases for, say, a gas. More will be said about this later. Mostly we will use the Centigrade or Celsius scale which differ only slightly in that the Celsius scale uses the Triple Point of water (where the solid, liquid, and gas phases coexist) instead of the freezing point of water.

Heat Energy

Heat is a form of energy and it is measured in Joules (just like Work, Kinetic Energy, Potential Energy, etc.) Originally heat was thought of as a kind of fluid (named "caloric") but it had to have some strange properties (e.g. caloric had to be massless since the mass of a material does not change as the temperature changes). A crucial experiment was done by Benjamin Thompson (Count Rumsford when he did his work for the German military in 1700s but originally an American). He was in charge of boring holes in metal for cannons and he observed that the work of boring the hole was converted into heat because water was used to cool the metal and the water boiled off. In fact, he realized that you could produce an infinite amount of heat this way by just doing more work in boring the cannon hole. The (incorrect) idea that heat is a fluid has a residual concept in that the unit of heat that is sometimes used is called the calorie (for example, food energy is measured in kilocalories). While the calorie is still used at times, the English scientist Joule realized that the same unit (now called the Joule) should be used for heat energy since it is just a form of energy and the conversion factor is

1 calorie = 4.18 Joules

0th Law of Thermodynamics

It seems this law was an afterthought. Consider two objects--say two blocks of copper--of different masses, and suppose they are initially not in contact. Then bring the two blocks together so they touch. If the temperature of block A is greater than the temperature of block B, then we know that when the two blocks are brought into contact, heat will flow from A to B. We know heat "flows" (again this is a residue of the caloric theory) and we know this because the temperature of A decreases and the temperature of B increases.

The Before Situation $T_A > T_B$

Block A   Block B

The After Situation
→ Heat Flow Q

A   B
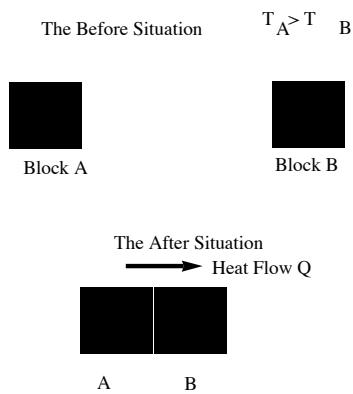
So temperature tells us which way heat Q will flow, and this is the 0th Law of Thermodynamics:

If two objects are of different temperatures when they are spatially separated, then when they are brought into thermal contact, heat flows from the hotter object to the colder object. Temperature is an indicator or predictor of the direction of heat flow. If the two objects originally had the same temperature, then no heat flows when they are brought into contact.

So temperature and heat are different but *sometimes* related concepts. Heat is energy and temperature is not. Under some circumstance, when heat is added to a substance, then the temperature rises. (For example, if heat is added to the water in a teapot on the stove and the water is not boiling, then the temperature of the water rises.) Sometimes when heat is added to a substance, the temperature does NOT rise. (For example, if the water in the teapot is at the boiling point of water, which is 100°C, then adding heat does NOT change the temperature from 100°C.) This is called a phase transition (from a liquid phase to a gas phase). Adding heat to a material at a phase transition does not cause its temperature to rise.

Heat Capacity and Specific Heat

Suppose you have a beaker of water on a stand above a Bunsen burner. After a time, the temperature of the water rises (if you are not at a phase transition), and we say that this is because heat was transferred from the burning flame to the water. Usually there is a linear connection between the heat Q added in Joules and the temperature change ΔT and this is written as

$$Q = C \, \Delta T$$

where the constant C is called the heat capacity. Actually, if you have more mass (m) of a

$$1 \text{ kilocalorie} / (\text{kilogram} \times °C)$$

1 kilocalorie

substance, a larger amount of heat Q is required to change the temperature say $\Delta T = 1°C$. This is taken into account by writing

$$Q = m \, c \, \Delta T$$

where the small letter c is called the "specific heat" and has units 1 kilocalorie / (kilogram×°C). The specific heat c depends upon the substance. For example, the specific heat of copper is 0.093, the specific heat of wood is 0.4, and the specific heat of aluminum is 0.22, in the above units. There is a table of specific heats of various materials in the textbook in both kilocalories and kiloJoules. The specific heat of liquid water is defined as

$$c = \frac{1 \text{ kilocalorie}}{\text{kilogram×°C}} = 1$$

and the equation $Q = m \, c \, \Delta T$ is then used to define the kilocalorie since mass m and temperature T have separate definitions. The specific heat of water depends on its phase. Even though the specific heat of liquid water is c=1, steam, which is the gas phase of water, has a specific heat of 0.48 kilo-cal./kg×°C, and ice, which is the solid phase of water, has a specific heat of 0.50 kilo-cal./kg×°C. If you were to add 1 calorie of heat to two different substances, the substance with the smaller specific heat would have a greater rise in temperature. Hence wood (c=0.4) would have a smaller temperature rise than copper (c=0.093) if the same amount of heat were added to each.

Heat of Fusion

Suppose you have a cup of iced tea with ice floating on the surface of the tea. At equilibrium, the temperature of the ice and water mixture is 0°C. Heat enters the cup through the sides and top, but the effect is just to melt the ice. The temperature of the iced tea remains 0°C until all the ice melts,

L_{fusion}

L_{fusion}

L_f

and then the temperature rises. The amount of heat Q necessary to melt Δm grams of ice is called

the heat of fusion of ice L_{fusion} and

$$Q = L_{fusion} \Delta m$$

Notice that temperature does NOT appear in this equation. Adding heat has not changed the

temperature of the tea and ice mixture. The effect of adding heat Q has been to melt some ice Δm.

This is another example of the difference between heat Q and temperature T; there is no

connection between heat and temperature at a phase transition. The heat of fusion is L_f=80 cal/gm

for ice, but other substances have different heats of fusion. (See the table in your book.)

Heat of Vaporization

When water vaporizes at 100°C, heat is added to the water without changing the temperature of

the water. This is another example of a phase transition--this time from liquid to vapor. The

associated $L_{vaporization}$ is given by

$$Q = L_{vaporization} \Delta m$$

Again there is no connection between heat Q and temperature T. For the water to make the

transition to steam, the heat of vaporization is L_V=540 cal/gm. Other substances have different

heats of vaporization. (See the table in your book.)

Example of Using Heat of Fusion

Suppose you have 40 grams of ice in water and the mixture is in equilibrium at T=0°C. How much

heat is required to melt 15 grams of the ice?

ANSWER: Q=80 cal/gm×15 grams = 1200 calories.

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80 * 15.

1200.
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Example of Using Heat of Vaporization

Suppose you have 15 grams of liquid water at T=100°C. How much heat is required to boil off all 15 grams of water entirely into 15 grams of steam or water vapor which is the same thing?

ANSWER: Q=540 cal/gm×15 grams = 8100 calories. (This is huge compared with the previous example; it clearly costs much more to vaporize water than to freeze it.)

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540 * 15.
8100.
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An Example of Using Specific Heat

How much heat Q is required to raise the temperature of 10 grams of lead from 20°C to 100°C?

The specific heat of lead is c=0.031 cal/gm×°C.

Answer: Q=mcΔT=10 gm×0.031 cal/(gm×°C)×(100°C-20°C)=24.8 cal

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10 * 0.031 * (100 - 20)
24.8
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Since 4.2 Joules = one cal, this heat is equivalent to Q=104 Joules.

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24.8 * 4.2
104.16
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Another Example of Using Specific Heats

Suppose you put 18 grams of ice at 0°C in 150 grams of Coca-cola at 25°C. What is the eventual temperature of the ice-Coke mixture? The basic idea is that the heat gained by the ice equals the heat lost by the Coke. This is conservation of heat energy. You have take into account the possibility that all the ice melts and the final temperature T of the Coke-ice mixture is greater than 0°C. The specific heat of Coke is the same as water (c_{Coke}=1.00 cal/(gm×°C)). Additionally, the heat of fusion of ice is L_{fusion}= 80 cal/gm.

ANSWER: $L_{fusioin-ice}^{gained} \Delta m + (mc\Delta T)_{water}^{gained} = (mc\Delta T)_{coke}^{lost}$

18 gm×80cal/gm + 18 gm×1 cal/(gm×°C)×(T - 0°C) = 150 gm×1.00 cal/(gm×°C)×(25°C - T)

Solving we get for the final temperature T=13.75 °C

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Solve[{18 * 80 + 18 * T == 150 * (25. - T)}, {T}]

{{T → 13.75}}
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Yet Another Example:

Suppose 100 grams of water and 400 grams of ice are in equilibrium at T=0°C inside a can that is also at T=0°C, and that the can has a specific heat of 0.20 cal/(gm×°C). Suppose a 300-gram chunk of metal at temperature T and with a specific heat of c=0.10 cal/(gm×°C) is added to the mixture and everything comes to equilibrium at 10 °C. What is the initial temperature T of the metal chunk?

ANSWER: The heat lost by the chunk of metal equals the heat gained by the ice in melting plus the heat gained by the melted ice together with the original water plus the heat gained by the can.

$$(mc\Delta T)^{\text{lost}}_{\text{chunk}} = \left(L^{\text{gained}}_{\text{fusion-ice}} \Delta m\right) + (mc\Delta T)^{\text{gained}}_{\text{water}} + (mc\Delta T)^{\text{gained}}_{\text{can}}$$

0.10 cal/(gm×°C)×300 gm ×(T-10°C)=100 gm×80cal/gm+500 gm×1.0 cal/(gm×°C)×(10°C-0°C)+ 70 gm×0.2 cal/(gm×°C)×(10°C-0°C) and using *Mathematica* to solve for T we get 448°C for the initial temperature of the metal chunk.

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Clear[T];
Solve[{0.10 * 300. * (T - 10) == 100 * 80. + 500 * 1 * (10 - 0) + 70 * 0.2 * (10 - 0)}, {T}]

{{T → 448.}}
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The Ideal Gas Law and the Absolute Zero of Temperature

Suppose you have a fixed amount (that is, so many grams) of nitrogen gas in a container of fixed volume V and you put the container with the nitrogen above a Bunsen burner. Also suppose there is a mercury thermometer in contact with the gas to measure the gas temperature T and that there is a device (not unlike the pressure gauge for a bicycle tire) for measuring the nitrogen gas pressure P. Then it is experimentally observed that as the temperature T of the gas increases, the pressure P of the gas increases and the connection is a linear one, $P = \kappa T$ where κ is a constant. (You probably have observed this effect with the gas pressure of a car tire, which increases on a hot day, given that the volume of the container is more or less constant.) A graph of the data you could take might appear
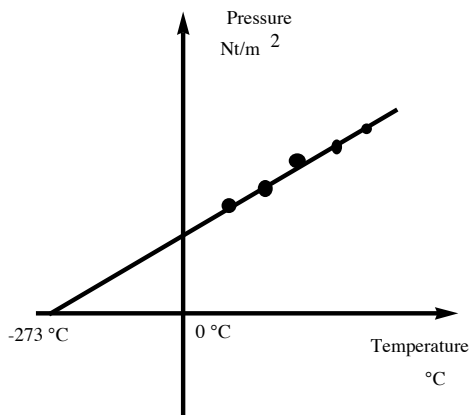
The data you take is at a temperature greater than T=0°C and is indicated by the dots on the line, which is a best fit of the data. The relation P=α T + β is called "Charles' Law" after its discoverer. (Note α is the slope of the above graph and the y intercept is P=β when T=0°C). The interesting thing is that extrapolation of this linear graph predicts there will be a point where the pressure of the gas is zero, that is P=0 and the temperature where that occurs is T = -273°C. Since presumably you cannot have a negative pressure P, this temperature T = -273°C is absolutely the smallest temperature nitrogen (or any other substance) can have. This temperature is called "the absolute zero" of temperature. (Today, because we know atoms exist, this result is interpreted as follows: The motion of the gas atoms is zero when T=0, and since pressure is the result of gas atoms hitting the walls of the container (and the atoms are no longer moving), the pressure is zero.)

Lord Kelvin realized this experimental fact could be used to define a temperature scale having one of the two reference points as the absolute zero of temperature and he wrote

$$K = C + 273°C$$

where T is the Kelvin temperature and C is the Celsius temperature. Kelvin picked the size of his degrees to be the same size as the Celsius degrees. For example, when C=-273° then the Kelvin temperature is 0° and when C=0° at the freezing point of water then K=273°. The Kelvin temperature scale is also called the absolute temperature scale.

Question: How would Charles' Law appear if you used the Kelvin scale?

ANSWER: P = α K

Check: When C=-273 then K=0 and P=0. By the way, when you use the ideal gas law you must use temperature T measured in Kelvin degrees. Why? From now on, T will be the Kelvin temperature except for the temperature difference ΔT, which may be either Kelvin degrees or Celsius degrees since they have the same size. Charles' Law is usually written $\frac{P}{T} = \alpha$ with T the temperature in Kelvin degrees.

Boyle's Law

Again let us suppose you have a fixed amount (so many grams) of nitrogen gas in a container but the volume V of the container is not fixed. The temperature, however, is fixed in this experiment. (This could be achieved by placing the container in a large tank of water that has a fixed temperature. Then heat could flow between the water and the gas, maintaining a constant temperature for the gas.) It is experimentally observed that the pressure P of the gas increases when the volume V of the gas container is made smaller. (You basically do this experiment when you squeeze a balloon.) The pressure P and volume V are inversely related P=$\frac{\epsilon}{V}$ because a smaller gas volume V means a larger gas pressure P. This is called Boyle's Law and is usually written PV=ϵ where ϵ is a constant.

The Ideal Gas Law

When the pressure P, temperature T, and volume V are allowed to vary, then a combined so-called Ideal Gas Law holds

$$\frac{PV}{T} = N \, k_B$$

where N is the number of molecules of gas, which was a fixed amount in both Charles' and Boyle's Laws.

k_B=1.38 × 10^{-23} Joules/°K is called the Boltzmann constant and is experimentally determined. The unit of k_B might seem a little strange but they work out. The °K are OK since they are in the denominator on both sides of the equation. The Joule=Nt×m=(Nt/m^2)×m^3 and pressure P is measured in Nt/m^2 while volume V is measured in m^3, so the units work out.

Example of the Ideal Gas Law

What is the density n of a gas of atoms or molecules under ordinary circumstances? Suppose the

pressure P=atmospheric pressure and one atm. = 10^5 Nt/m^2 so P= 10^5 Nt/m^2 . Suppose the

temperature of the gas is "room temperature" or 20°C, which is T=293°K. The Boltzmann constant

is k_B=1.38×10^{-23} J/°K, so from the ideal gas law the density n=N/Ω where the volume of the gas is

Ω=L^3 if you have a cubic box of side L. Using this notation, the ideal gas law is

$$P\Omega = Nk_BT \ \ \text{or} \ \ n = \frac{N}{\Omega} = \frac{P}{k_B T}$$

Substitution of the numerical values yields

$$n = \frac{10^5 \, \text{Nt}/m^2}{1.38\times10^{-23} \, J/\circ K \times 293 \, \circ K.} = 2.47 \times 10^{25} \text{ molecules/}m^3.$$

and using *Mathematica* we have

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    10⁵
─────────────────
1.38 * 10⁻²³ * 293
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$$2.47317 \times 10^{25}$$

Question: How far ℓ are molecules apart in a gas on average?

You can imagine a cube of volume ℓ^3 which has just one molecule in it so the density of the gas in this one cube is $n=1/\ell^3$ and this must equal the density n of the gas overall. Solving for ℓ yields

$$\ell \; = \; \frac{1}{n^{\frac{1}{3}}}$$

which is the inverse of the cube root of the density n. Substitution of the numerical value for n just obtained above you get with *Mathematica*

$$\frac{1}{\left(2.4 * 10^{25}\right)^{\frac{1}{3}}}$$

3.46681×10^{-9}

so the distance between molecules is about 3.5×10^{-9} m. How big is this? You can compare ℓ with something you know like the size of an atom, which is roughly 10^{-10} m $= 10^{-8}$ cm $= \text{Å}$ which is an Angstrom. So $\ell/\text{Å} = 35$ and the distance molecules are apart is about 35 times the size of a molecule, and this means there is a lot of empty space in a gas.

$$\frac{3.47 * 10^{-9}}{10^{-10}}$$

34.7