Contents

Chapter 1

The Physics of Gases

Now, let's say you start to heat the helium inside the balloon. As the temperature goes up, the molecules inside will start to move faster.

Remember that the kinetic energy of an object with mass m and velocity v is given by

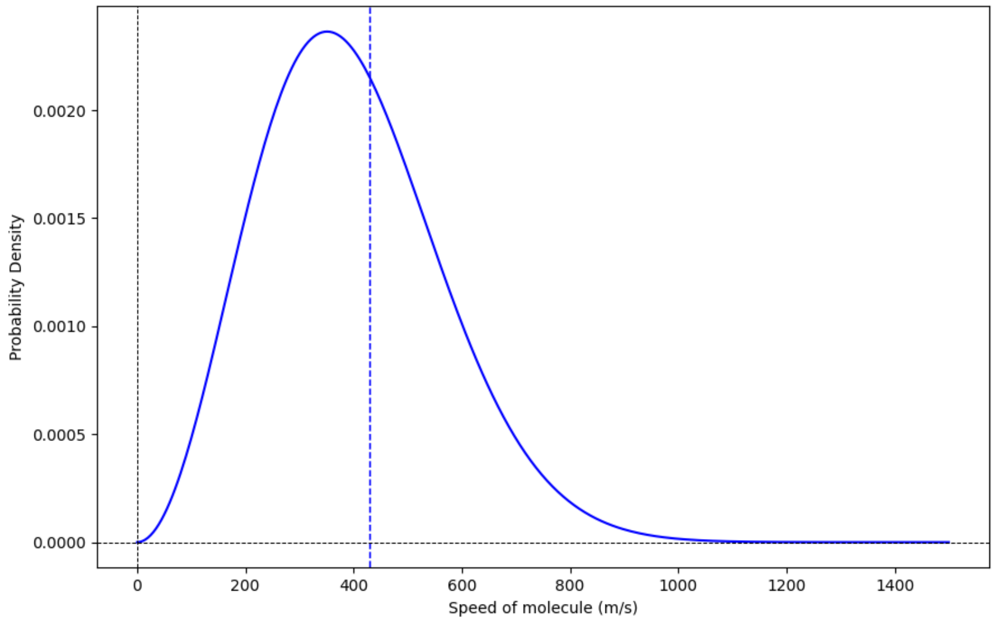
$$k = \frac{1}{2}mv^2$$

So, you could say "As the temperature of the gas increases, the kinetic energy of the molecules increases." But a physicist would say "The temperature of the gas is how we measure its kinetic energy."

1.0.1 A Statistical Look At Temperature

If you say "This jar of argon gas is 25 degrees Celsius," you have told me about the *average* kinetic energy of the molecules in the jar. However, some molecules are moving very slowly. Others are moving really, really fast.

We could plot the probability distribution of the speeds of the molecules. For argon at 25 degrees Celsius, it would look like this:



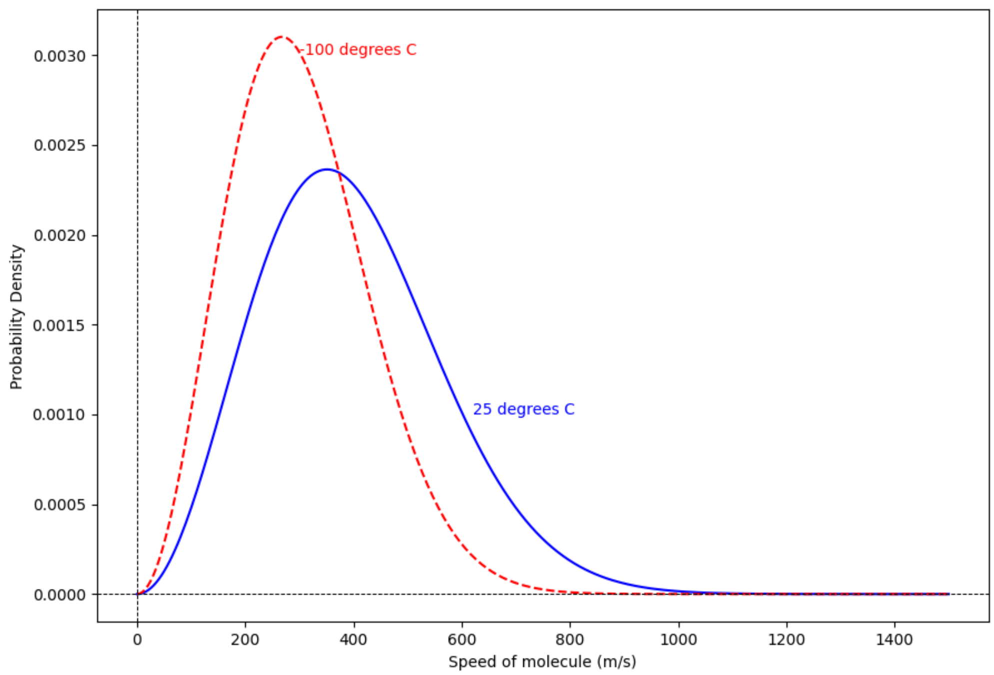
The temperature, remember, is determined by the average kinetic energy of the molecules. Some molecules are moving slowly, and have less kinetic energy than the average. Some molecules are moving very quickly, and have more kinetic energy. The dotted line is the divider between the two groups: molecules moving at speeds to the left of the line have less kinetic energy than average; those on the right have more kinetic energy than average.

Where is that line? That is the RMS of the speeds of the molecules. That is, if we measured all the speeds of all the molecules $s_1, s_2, s_3, \ldots, s_n$, that line would be given by the root of the mean of the squares:

$$v_{rms} = \sqrt{\frac{1}{n}\left(s_1^2 + s_2^2 + s_3^2 + \ldots s_n^2\right)}$$

If you have the same gas at a lower temperature, the distribution shifts toward zero:

Here is probability distribution of molecular speeds for argon gas at 25 degrees and -100 degrees Celsius.



1.0.2 Absolute Zero and Degrees Kelvin

If you keep lowering the temperature, eventually, all the molecules stop moving. This is known as *absolute zero* — you can't make anything colder than absolute zero. Absolute zero is -273.15 degrees Celsius.

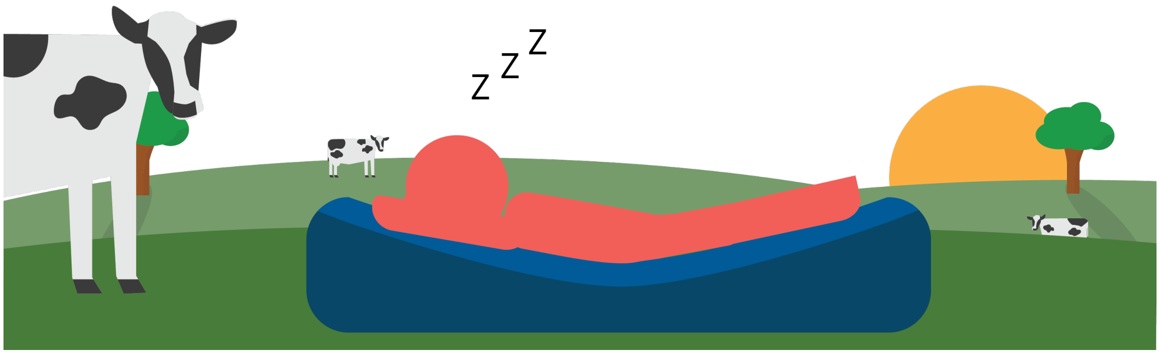
In addition to Celsius and Fahrenheit, there is a third temperature system: Kelvin. Kelvin has the same scale as Celsius, but it starts at absolute zero. So, 0 degrees Celsius is 273.15 degrees Kelvin, and 100 degrees Celsius is 373.15 degrees Kelvin.

Any time you are working with the physics of temperature, you will use Kelvin.

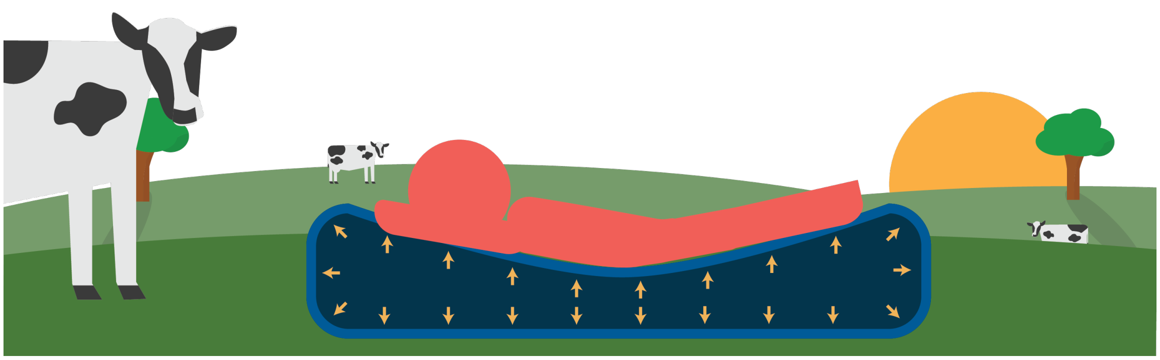
Sometimes, when reading about gases, you will see "STP" which stands for "Standard Temperature and Pressure." STP is defined to be 0° Celsius and 100 kPa.

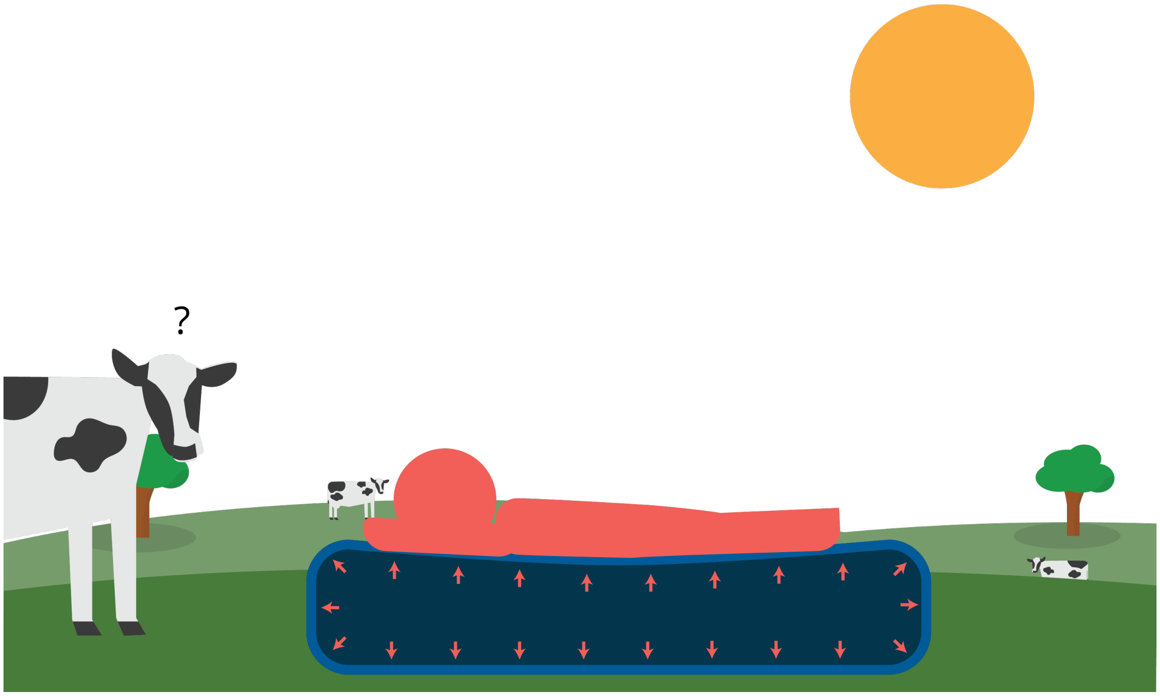
1.1 Temperature and Volume

Let's say you have a half-full air mattress in a field with a person lying on it around dawn. The weight of the person will keep the pressure of the air inside constant (or pretty close).



The molecules in the mattress are not entering or leaving that mattress. However, as the sun rises, the air inside will get warmer and expand. The person will be gently lifted by the expanding air. You might wonder: how much will the air expand?





If you have constant pressure and and a constant number of molecules, the volume of the gas is proportional to the temperature in Kelvin:

$$V \propto T$$

Exercise 1 Temperature and Volume

Working Space

At dawn, the air inside mattress at dawn has a volume of 1000 liters and a temperature of 12 degrees Celsius.

At noon, that same air has a temperature of 28 degrees Celsius. The pressure on the gas has not changed at all.

What is the volume of the gas at noon?

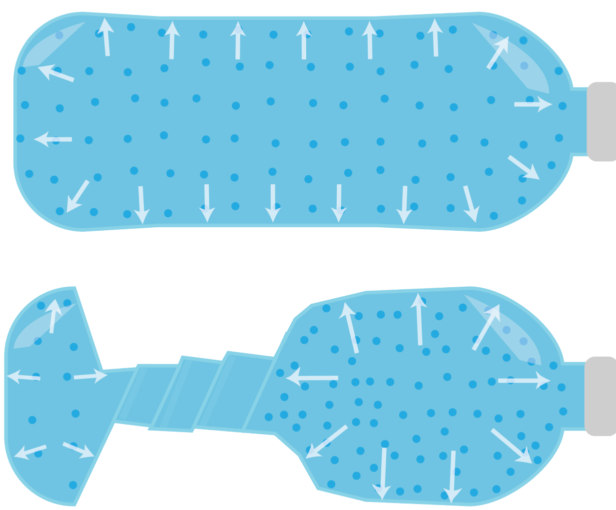
Answer on Page 45

Note: Volume and temperature are only proportional as long as the substance is a gas. We will talk about liquids and solids soon.

1.2 Pressure and Volume

As you increase the pressure on a gas, the molecules will get pushed closer together, and the volume will decrease.

For example, if you put the cap on an empty plastic bottle and squeeze it. As you put the gas inside the bottle under pressure, its volume will decrease.



If you keep the number of molecules and the temperature constant, the pressure of the gas and its volume are inversely proportional:

$$P \propto \frac{1}{V}$$

"But," you say with disbelief, "if I increase the pressure on my empty water bottle from 5 kPa to 10 kPa, the volume inside won't decrease by half!"

Don't forget that the air inside the bottle is under 101 kPa of atmospheric pressure before you even start to squeeze it.

Exercise 2 Temperature and Volume

Working Space

At an altitude where the atmospheric pressure is 100 kPa, you seal air in a 1 liter water bottle.

Squeezing the water bottle, you raise the internal pressure by 20 kPa What is the volume inside the bottle now?

Answer on Page 45

1.3 The Ideal Gas Law

You are gradually getting an intuition for the relationship between the number of molecules, the volume, the pressure, and the temperature of a gas. We can actually bring these together in one handy equation.

Ideal Gas Law

$$PV = nRT$$

where:

- P is the pressure in pascals
- V is the volume in cubic meters
- n is the number of molecules in moles
- R is the molar gas constant: 8.31446
- T is the temperature in Kelvin

(You can remember this as the ”Pivnert.”)

From the name, you might predict the following: The Idea Gas Law is not 100% accurate. However, for most purposes, it works remarkably well.

Notice that the ideal gas law says nothing about what kind of gas it is; it works regardless.

Exercise 3 Ideal Gas Law

You have a cylinder containing O_2. The chamber inside has a radius of 12 cm and a length of 50 cm. The temperature inside the cylinder is 20 degrees Celsius. The pressure inside the tank is 600 kPa.

How many moles of O_2 are inside?

Working Space

Answer on Page 45

1.4 Molecules Like To Stay Close to Each Other

When two molecules get close to each other a few things can happen:

- They can under go a chemical reaction: electrons are exchanged or shared and a different molecule or molecules come into existence. This is the realm of chemistry, and we won't go into it in this course.
- One or both of them have so much kinetic energy that they just pass each other or bounce off each other. This is what happens in a gas.
- The two molecules can ”stick” together. This is what happens in a liquid or a solid.

Why do they stick together if they aren't combined in a chemical reaction?

First, they don't get *too close*. If they get too close, their electron clouds repel each other with a strong force. This is what happens in a gas when two molecules bounce off of each other.

However, if the molecules are quite close to each other, there are forces that will attract them toward each other. These intermoleculare forces are beyond the scope of this course, but they called Van der Waals forces and hydrogen bonds. The strength of these forces vary based on the two molecules involved.

Which is why some of the matter around you is in gas form (molecules that don't stick together at the temperature and pressure you are living in because they have weak attractive forces) and some is non-gas (gangs of molecules with stronger attraction that makes them clump together as a liquid or a solid at that same temperature and pressure).

However, what if we change the temperature and pressure? We can change if and how the molecules clump together. This is known a *phase change*; We will cover it soon.

Chapter 2

Kinetic Energy and Temperature of a Gas

As mentioned in the previous chapter, for a particular gas, the temperature (in Kelvin) is proportional to the average kinetic energy of the individual molecules.

Perhaps you want to warm 3 moles of helium gas (trapped in a metal cylinder) from 10 degrees Celsius to 30 degrees Celsius. How would you compute exactly how many Joules of energy this would require?

The amount of energy necessary to raise one mole of a molecule by one degree is known as *molar heat capacity*. (The molar heat capacity of liquid water, for example, is 75.38 J per mole-degree.)

With gases, there are actually two different possible situations:

1. Constant volume: As you heat the gas, the pressure and the temperature increase. This molar heat capacity is usually denoted as $C_{V,m}$.
2. Constant pressure: As you heat the gas, the temperature and the volume increase. This molar heat capacity is usually denoted as $C_{P,m}$.

All gases made up of one atom (Helium, for example, is a monoatomic gas.) have the same values for $C_{V,m}$ and $C_{P,m}$:

$$C_{V,m} = \frac{3}{2}R \approx 12.47 \text{ Joules per mole-degree}$$

$$C_{P,m} = \frac{5}{2}R \approx 20.8 \text{ Joules per mole-degree}$$

(Remember from last chapter that R is the ideal gas constant ≈ 8.31446 Joules per mole-degree.)

Exercise 4 Warming Helium

Working Space

You have 3 moles of helium.

1. How many Joules would be required to warm 3 moles of helium gas by 20 degrees Celsius at constant volume?
2. How many Joules would be required to warm 3 moles of helium gas by 20 degrees Celsius at constant pressure?

Answer on Page 46

2.1 Molecule Shape and Molar Heat Capacity

We told you that gases made up of one atom have the same values for $C_{V,m}$ and $C_{P,m}$:

$C_{V,m} = \frac{3}{2}R \approx 12.47$ Joules per mole-degree

$C_{P,m} = \frac{5}{2}R \approx 20.8$ Joules per mole-degree

For any molecule, it is generally true that

$$C_{P,m} \approx C_{V,m} + R$$

It is also true that for any molecule, there is some integer d such that

$$C_{V,m} \approx \frac{d}{2}R$$

For example, for all monoatomic gases, $d = 3$. For diatomic gases (like N_2 and O_2, d is 5.

d is known as the *degree of freedom* of the molecule. When you study chemistry, they will teach you to predict d based on the shape of the molecule.

Here are the relevant numbers for some gases you are likely to work with:

Gas	type	$C_{V,m}$	$C_{P,m}$	d
He	monoatomic	12.4717	20.7862	3
Ar	monoatomic	12.4717	20.7862	3
O_2	diatomic	21.0	29.38	5
N_2	diatomic	20.8	29.12	5
HO_2 (water vapor)	3 atoms	28.03	37.47	7
CO_2	3 atoms	28.46	36.94	7

2.2 Kinetic Energy and Temperature

For a sample of a gas, we can calculate its kinetic energy based on its molar heat capacity, the number of molecules, and the temperature:

$$E_K = C_{V,m} n T$$

where

- E_K is the kinetic energy in Joules
- $C_{V,m}$ is the molar heat capacity of the gas at constant volume
- n is the number of molecules in moles
- T is the temperature in Kelvin

Exercise 5 Warming Helium Revisited

Working Space

How much kinetic energy does 3 moles of helium have at 10 degrees Celsius?

How much kinetic energy does 3 moles of helium have at 30 degrees Celsius?

What is the difference?

Answer on Page 46

2.3 Why is $C_{V,m}$ different from $C_{P,m}$?

What if, instead of keeping the volume constant while we heat the molecules in the helium tank, we keep the pressure constant and let the gas expand? The change in kinetic energy is the same: 748 Joules.

However, we know that the molar heat capacity if we keep pressure constant is $\frac{5}{2}R$, so heating will require $\frac{5}{2}R(3)(20) = 1247$ Joules.

What happened to the 499 missing Joules!? Thermodynamics tells us energy is neither created nor destroyed, so it must have gone somewhere.

That energy was used pushing against the pressure as the gas expanded. For example, maybe the sample was in a balloon in space — the extra energy stretched the surface of the balloon.

The 499 Joules were converted into potential energy.

2.4 Work of Creating Volume Against Constant Pressure

Let's imagine that you had a total vacuum (zero pressure) with a piston. As you pulled the piston out, you would be pulling against the atmospheric pressure. How much energy would that require?

If you increased the volume of the vacuum by V against a pressure of P, you would do

VP work.

Let's check to make sure the 499 Joules mentioned above makes sense with this in mind.

No initial pressure was given in the problem, so let's just make one up and see how things work out: 100 kPa. Using the ideal gas law, the initial volume would be:

$$V_1 = \frac{nRT}{P} = \frac{(3)(8.31446)(283.15)}{100,000} = 0.07063 \text{ cubic meters}$$

The volume after we heated the gas and let it expand against 100 kPa would be:

$$V_2 = \frac{nRT}{P} = \frac{(3)(8.31446)(303.15)}{100,000} = 0.07562 \text{ cubic meters}$$

So, the volume increased by $0.07562 - 0.07063 = 0.00499$ cubic meters. Multiplying that by 100,000 pa, we get 499 Joules, as we expected!

2.5 Why does a gas get hotter when you compress it?

Now, imagine that there is gas inside the piston and you push on the piston to compress that air. The work that you do is converted into kinetic energy, and that kinetic energy raises the temperature of the gas.

SFor example, if you had two moles of argon gas in the piston, and you pushed the piston 0.1 meters with an average force of 50 newtons, you will have done 5 Joules of work.

How much would 5 Joules raise the temperature of 2 mole of a monoatomic gas?

$$\Delta T = \frac{5}{(2)(C_{V,m})} = 0.2^\circ \text{ Kelvin}$$

It works both ways: Compression makes a gas hotter; decompression makes a gas colder. You can sometimes experience the heat of compression when you pump up a bicycle tire — as you pump the tire will get warmer.

If you compress or decompress a gas without letting any heat enter or depart, we say the compression or decompression was *adiabatic*. In order to solve any interesting problems about heating/cooling due to compression/decompression, you will need to assume the process was adiabatic.

When a spacecraft enters the atmosphere, it has to deal with a lot heat. Some people assume that heat is due to friction of the air rubbing against the spacecraft at over 7,000 meters per second. Actually, most of the heat is due to the compression of the air as it gets pushed out of the way of the spacecraft.

2.6 How much hotter?

Let's say you have an accordion-like container filled with helium at 100 kPa (about 1 atmosphere) and 300 degrees Kelvin. It holds 2 cubic meters. You then you put it in a vice and quickly compress it down to 0.5 cubic meters. Assuming it was adiabatic, how hot would the gas inside be after the compression?

Here is the challenging part: As you crush the container, the temperature and the pressure in the container are both increasing. So, as you go, it gets harder and hard to crush. Each milliliter of volume that you eliminate requires a little more work than the milliliter before.

Let's simulate the process in Python, after which we will give you the formula.

In the simulation, you will start with an initial volume of 2 cubic meters and crush it down to 0.5 cubic meters in 40 steps. At each step you will recalculate the temperature and pressure.

Next, you will plot the results. Make a file called `gas_crunch.py`:

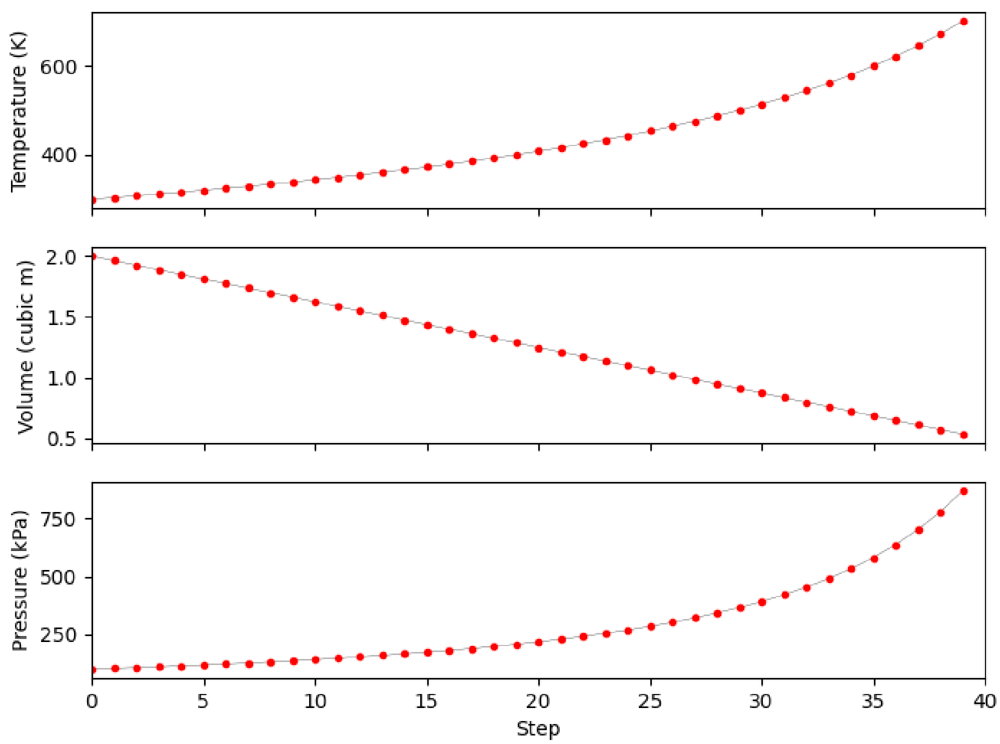
```
import numpy as np
import matplotlib.pyplot as plt

V_initial = 2.0 # cubic meters
V_final = 0.5 # cubic meters
step_count = 40 # steps

T_initial = 300.0 # kelvin
P_initial = 100000 # pascals

# Constants
R = 8.314462618 # ideal gas constnt
C_v =  3.0 * R / 2.0 # molar heat capacity (constant volume)

# Compute the number of moles
n = P_initial * V_initial/(R * T_initial)
print(f"The container holds {n:.2f} moles of helium")

# How much volume do we need to eliminate in each step?
# (in cubic meters)
step_size = (V_initial - V_final) / step_count
```

```
# For recording the state for each step
data_log = np.zeros((step_count, 3))

# Variables to update in the loop
V_current = V_initial
T_current = T_initial
P_current = P_initial

for i in range(step_count):
    # Record the current state
    data_log[i,:] = [T_current, V_current, P_current/1000.0]

    # Find how much energy to make the step at the current pressure
    E_step = step_size * P_current

    # Find how big the change in temperature will be from that energy
    delta_T = E_step / (n * C_v)

    # Update the current temperature, volume, and pressure
    T_current += delta_T
    V_current -= step_size
    P_current = n * R * T_current / V_current

print(f"Iterative:{T_current:0.3f} K, {V_current:0.3f} m3, {P_current/1000.0:0.3f} kPa")

fig, axs = plt.subplots(3,1,sharex=True, figsize=(8, 6))
axs[0].set_xlim((0,step_count))
axs[0].plot(data_log[:,0], 'k', lw=0.2)
axs[0].plot(data_log[:,0], 'r.')
axs[0].set_ylabel("Temperature (K)")

axs[1].plot(data_log[:,1],'k', lw=0.2)
axs[1].plot(data_log[:,1], 'r.')
axs[1].set_ylabel("Volume (cubic m)")

axs[2].plot(data_log[:,2], 'k', lw=0.2)
axs[2].plot(data_log[:,2], 'r.')
axs[2].set_ylabel("Pressure (kPa)")

axs[2].set_xlabel("Step")

fig.savefig('tvpplot.png')
```

When you run this, you will see how many moles of gas there are and reasonable estimates of the temperature, volume, and pressure:

```
> python3 gas_crunch.py
The container holds 80.18 moles of helium
Iterative:733.499 K, 0.500 m3, 977.999 kPa
```

And a good plot of the intermediate values:

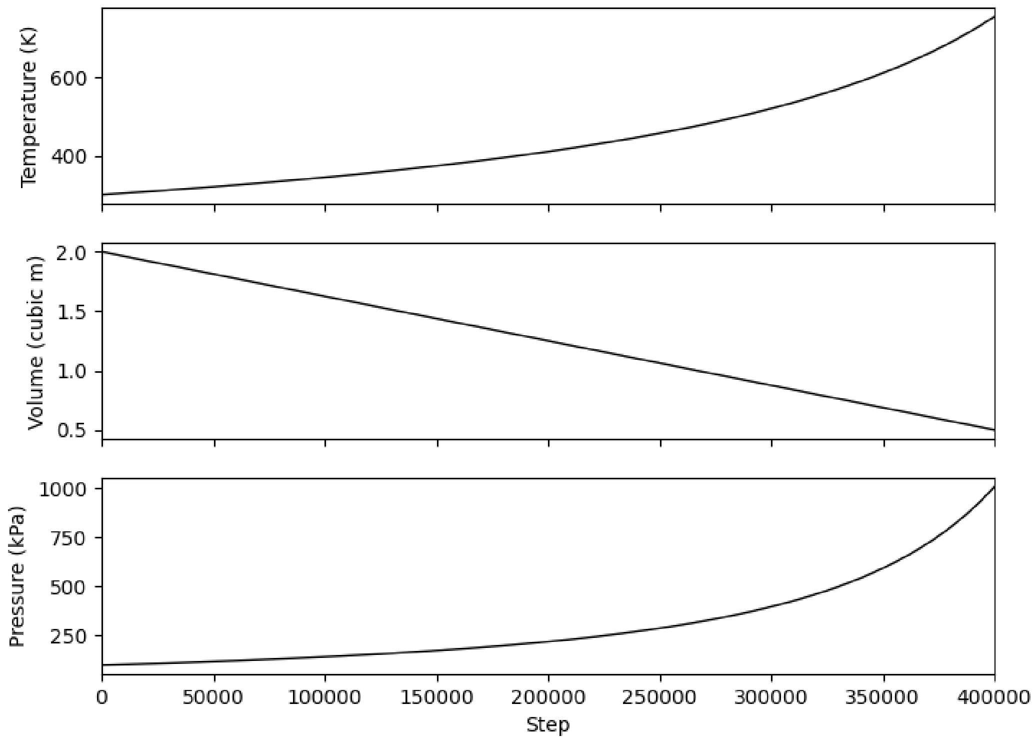


However, we will get better estimates if we break it up into 400 steps instead of 40. Change the line that defines the number of steps:

```
step_count = 400 # steps
```

Now the predicted temperature and pressure should be something like 753.603° K and 1004.803 kPa. (This is much closer to the correct result: :755.953° K and 1007.937 kPa.)

What if you break it into 400,000 steps? Now, the result should be really, really close to correct. And the plot is quite accurate:



(You can comment out the lines that make the red dots on the graphs. No one wants to see 400,000 red dots.)

It is inefficient to have to do long simulations to guess the final temperature and pressure. Fortunately, there are two handy rules you can use to skip this:

Adiabatic Compression and Decompression

Let

$$\gamma = \frac{C_{P,m}}{C_{V,m}}$$

In an adiabatic compression or decompression, P and V change, but

$$P\left(V^{\gamma}\right)$$

stays constant.

Also

$$T\left(V^{(\gamma-1)}\right)$$

stays constant

For a monoatomic gas:

$$\gamma = \frac{C_{P,m}}{C_{V,m}} = \frac{5}{3}$$

$$\gamma - 1 = \frac{2}{3}$$

Before the compression:

$$T\left(V^{(\gamma-1)}\right) = 300\left(2^{0.6667}\right) = 476.22$$

After the compression it has to be the same:

$$T\left(V^{(\gamma-1)}\right) = T\left(0.5^{0.6667}\right) = 476.22$$

Thus

$$T = 755.95^{\circ}\ \text{Kelvin}$$

We can then use the ideal gas law to solve for the final pressure:

$$P = \frac{nRT}{V} = \frac{(80.18)(8.31446)(755.95)}{0.5} = 1007937\ \text{pascals}$$

That iss hot! As you let it cool back down to 300 degrees Kelvin, how much heat would be released?

$$E = C_{V,m} n \Delta T = (12.47)(80.2)(755.95 - 300) \approx 456\ \text{kJ}$$

2.7 How an Air Conditioner Works

Once again, imagine the accordion-like container filled with helium. Let's say you walked it outside and compressed it from 2 cubic meters to 0.5 cubic meters in a vise. The container would get to 755.95 degrees Kelvin. You keep it compressed in the vise, but let it cool down outside. When it gets back to 300 degrees Kelvin, you walk it back inside.

Now, without letting any molecules in or out of the container, you release the vise. The gas is decompressed and gets very cold. How cold? Cold enough to accept about 456 kJ of kinetic energy from your house. That is, it would absorb heat from your house until the gas inside was the same temperature as your house.

So, you walk outside with your accordion and your vise, and repeat:

1. Compress the gas outside.
2. Let the hot gas cool down outside.
3. Walk the room-temperature compressed gas inside.
4. Decompress the gas inside.
5. Let the cold gas warm up inside.

You could keep your house cool on a hot day this way. This is not unlike how an air conditioner works.

There is a hose filled with refrigerant that does a loop:

- Outside, the refrigerant is compressed and allowed to cool to the outside temperature. (Usually there is a big fan blowing on a coil of refrigerant to speed the process.) Inside, the refrigerant is decompressed and allowed to warm to the inside temperature. (Usually there is a big fan blowing the air of the home past a coil of refrigerant to speed the process.)

In each pass of the loop, the refrigerant absorbs some of the kinetic energy from inside the house, and releases it on the outside.

This same mechanism can be used to heat your house. (Units that both heat and cool are known as *heat pumps*.) The heat pump does the process backwards: The hot compressed refrigerant cools down inside. The cold decompressed refrigerant warms up outside.

Chapter 3

Phases of Matter

You have experienced H_2O in three phases of matter:

- Ice is H_2O in the solid phase. At standard pressure, when the temperature of H_2O is below 0° C, it is a solid.
- Water is H_2O in the liquid phase. At standard pressure, when the temperature of H_2O is between 0° C and 100° C, it is a liquid.
- Water vapor (or steam) is the gas phase. At standard pressure, when the temperature of H_20 is above 100° C, it is a gas.

Let's look at some of the properties of the three phases:

Gas	Liquid	Solid
Assumes the volume and shape of its container	Assumes the shape, but not the volume, of its container	Retains its shape and volume
Compressible	Not compressible	Not compressible

3.1 Thinking Microscopically About Phase

As mentioned in an early chapter, there are intermolecular forces that attract molecules to each other. A pair of molecules will have very strong intermolecular forces or very weak intermolecular forces, depending on what atoms they are made of.

For example, two helium molecules are very weakly attracted to each other due to weak intermolecular forces. Two molecules of $NaCl$ (table salt) will experience very strong intermolecular attraction.

In a gas, the molecules have lots of room to roam and lots of kinetic energy: The intermolecular attraction has very little effect.

In a liquid, the molecules are sticking close together, but are still moving around, sort of like bees in a hive.

In a solid, the molecules are not changing their configuration, and the kinetic energy they have is just expressed as vibrations within that configuration. You can imagine them like eggs vibrating in a carton.

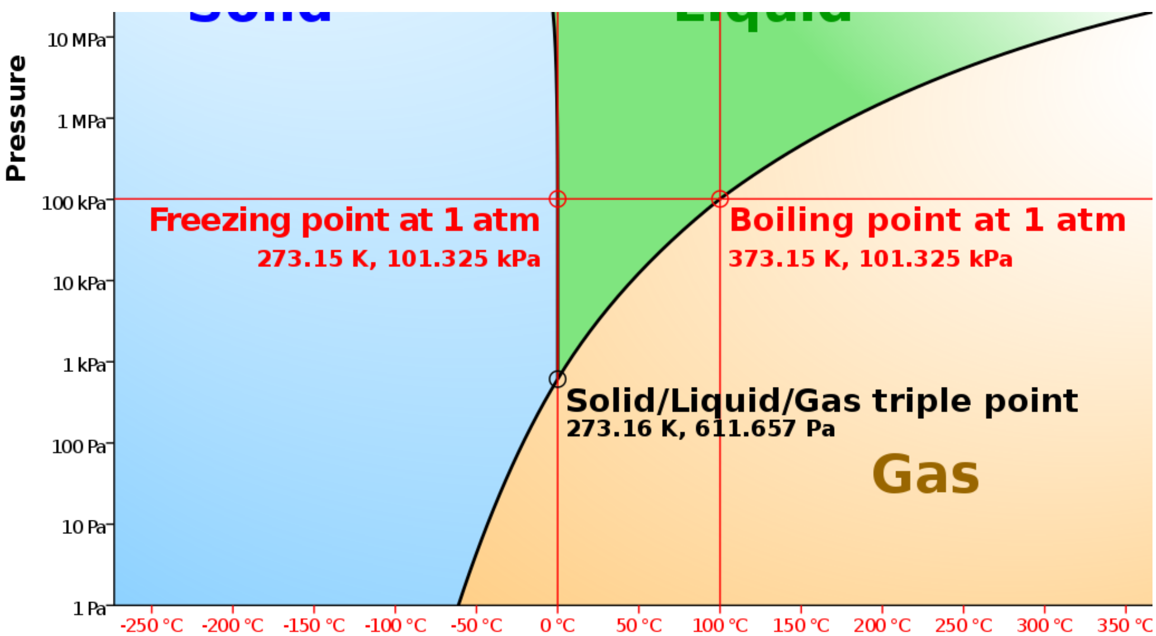
As you would expect, molecules with strong intermolecular attraction require more kinetic energy to change phases. For example, helium is a liquid below $-269\circ$ C. $NaCl$, on the other hand, is a liquid between 801° and $1,413^\circ$ C.

The temperatures I just gave you are at standard pressure (100 kPa or 1 atm). Pressure also has a role in phase change. In low pressure environments, it is much easier for the molecules to make the jump to being a gas.

For example, if you climb a mountain until the atmospheric pressure is 70 kPa, your water will boil at about 90° C.

If you rise in a balloon until the atmospheric pressure is 500 Pa, if your water is colder than -2° C, it will be ice. If it is warmer it will vaporize. There is no liquid water at 500 Pa!

For any molecule, we could observe its phase at a wide range of temperatures and pressures. This would let us create a phase diagram. Here is the phase diagram for H_2O:



(FIXME: This diagram needs to be recreated prettier.)

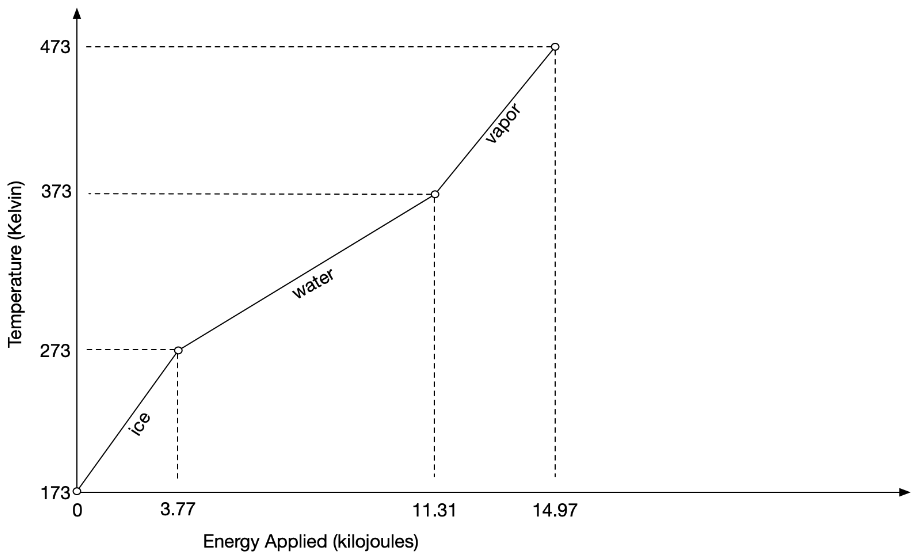
3.2 Phase Changes and Energy

The molar heat capacity of ice is about 37.7 J/mol-K. That is, it takes about 37.7 Joules of energy to raise the temperature of one mole of ice by one degree kelvin.

The molar heat capacity of liquid water is about 75.4 J/mol-K. For water vapor, it is about

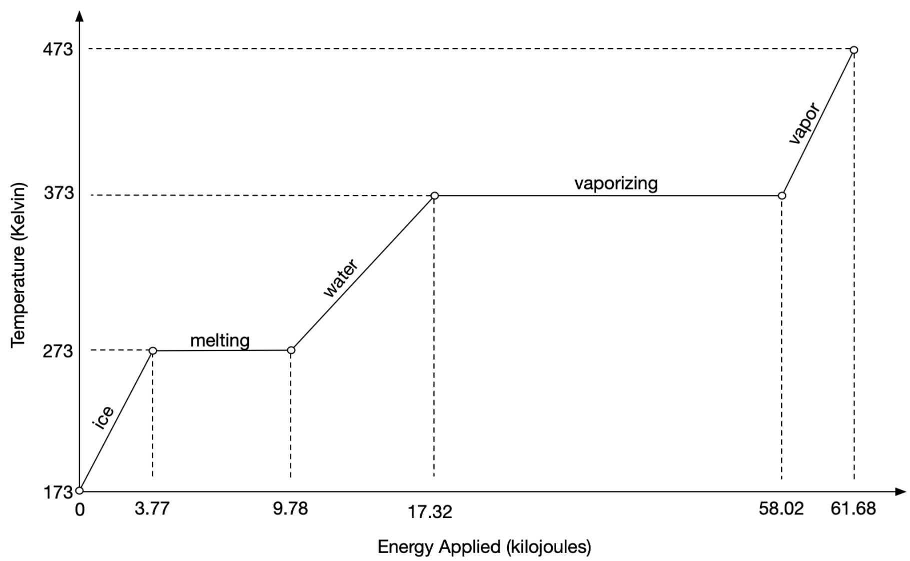
36.6 J/mol-K.

Imagine you have mole of ice at 173° K, and you are going to gradually add kinetic energy into it until you have steam at 473° K. You might guess (incorrectly) that the temperature vs. energy applied would look like this:



However, once molecules are nestled into their solid state (like eggs in cartons), it take extra energy to make them move like a liquid. How much more energy? For water, it is 6.01 kilojoules per mole. This is known as *the latent heat of melting* or *the heat of fusion*.

Similarly, the transition from liquid to gas takes energy. At standard pressure, converting a mole of liquid water to vapor requires 40. 7 kilojoules per mole. This is known as *the latent heat of vaporization*. So, the graph would actually look like this:



Note that just as melting and vaporizing require energy, going the other way (freezing and condensing, respectively) give off energy. Thus, we can store energy using the phase change.

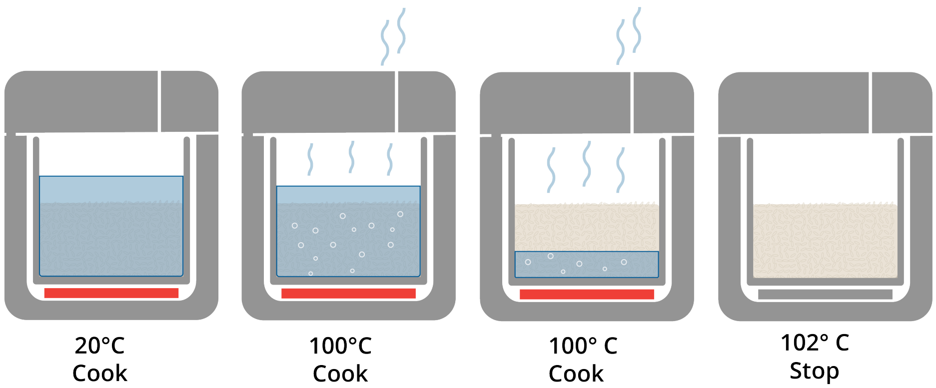
3.3 How a Rice Cooker Works

A rice cooker is a bowl with a lid and an electric heating element. You put rice and water into the bowl and turn on the heating element. The heating element pushes kinetic energy into the water, which gets warmer and eventually starts to boil.

How does the rice cooker know when to turn off (or at least down to a low-heat "keep warm" mode) before the rice starts to burn?

As long as there is a little liquid water in the bottom of the bowl, the rice won't burn, so the question is really "How does it know when there is no more liquid water in the bottom of the bowl?"

There is a mechanism (and there have been a few different versions of this mechanism) that monitors the temperature of the surface of the bowl. As long as there is liquid water in the bowl, it *cannot* go above 100° C! When all the water has been absorbed by the rice or turned to steam, the temperature rises above 100° C, and the mechanism cuts off the heat.


20°C
Cook
100°C
Cook
100° C
Cook
102° C
Stop

Exercise 6 Using Water For Thermal Energy Storage

Working Space

Tom is building a passive solar house; the front of his house is a greenhouse. He also likes to eat dinner in the greenhouse. He will have barrels (painted black) that hold 159 liters of water. His plan is to let the sun heat the barrels to 33° C by the time the sun goes down. (Any warmer and it would be unpleasant to eat dinner near them.)

At night, he will circulate air past the barrels and through his house. He is OK with the house and the barrels dropping to 17° C.

Looking at the insulation on his house and the expected nighttime temperatures, Tom estimates that he needs to store 300,000 kJ of energy in the barrels.

A mole of water is about 0.018 liters.

The molar heat capacity of water is about 75.38 J/mole-K.

How many barrels of water does Tom need to install in his greenhouse?

Answer on Page 47

Exercise 7 Using Mirabilite For Thermal Energy Storage

Working Space

Water barrels are going to take up too much of Tom's greenhouse!

There is a substance known as mirabilite, or Glauber's salt, or sodium sulfate decahydrate. It is relatively cheap to produce, and it has a melting point of 32.4° C.

The molar heat capacity of mirabilite is 550 J/mole-K.

The latent heat of melting mirabilite is 82 kJ per mole.

Mirabilite comes in a powder form. Assume that a mole of mirabilite occupies about 0.22 liters.

If Tom fills his barrels with mirabilite, how many barrels will he need?

Answer on Page 47

3.4 Thinking Statistically About Phase Change

We like to say simple things like "At 100° C, water changes to vapor." However, remember what temperature is: Temperature tells you how much average kinetic energy the water molecules have. The key word here is *average*; Some molecules are going faster than average and some are going slower.

A puddle in the street on a warm night will evaporate. It isn't 100° C. Why would the puddle turn to vapor?

While the *average* molecule in the puddle doesn't have enough energy to escape the intermolecular forces, some of the molecules do. When a molecule on the surface has enough velocity (toward the sky!) to escape the intermolecular forces, it becomes vapor and leaves the puddle.

What happens to the temperature of the puddle during this sort of evaporation? Temperature is proportional to the average kinetic energy of the molecules. If a bunch of molecules with a lot of kinetic energy leave, the average kinetic energy (of the molecules that remain) will decrease.

The most obvious example of this process is sweating: When your body is in danger of getting too hot, sweat comes out of your pores and covers your body. The fastest moving molecules escape your body, taking the excess kinetic energy with them.

3.4.1 Evaporative Cooling Systems

An evaporative cooling system (also called a ”Swamp Cooler”) uses this idea to cool air. You can imagine a fan drawing warm air through a duct from the outside. Before the air is released inside, it passes very close to a cloth that is soaked with water. The warm air molecules (which has a lot of kinetic energy) slam into the water molecules, some of which get enough kinetic energy to become vapor. The cool air and the water vapor then enter the room.

”Wait, wait, wait,” you say, ”The heat hasn’t gone away. It is just transferred into the water molecules.”

Remember that it takes 40.7 kilojoules to change a mole of liquid water at 100° C to water vapor at 100°. Escaping those intermolecular bonds takes a great deal of energy!

Thus, if a mole of water evaporates, it is because it has absorbed 40.7 kj of heat you can feel (*sensible heat*) and used it to liberate the molecules from their intermolecular bonds. For convenience, physicists call this *latent heat*.

3.4.2 Humidity and Condensation

When a puddle is evaporating on a warm day, there might be some water vapor already in the air. Even as the water molecules in the puddle are evaporating, some water molecules in the air are crashing into the puddle and become liquid again. (We say they *condensed*, thus the word *condensation* to describe the water that accumulates on a cold glass on a warm day.)

When there is a lot of water vapor in the air, the puddle will evaporate more slowly. In fact, if there is enough water vapor in the air, the puddle won’t evaporate at all. At this point, we say ”The relative humidity is 100%.” That is, relative to the amount of water the air will hold, it already has 100% that amount.

Neither sweating nor evaporative cooling systems work well when the relative humidity is high.

As the temperature goes up, the air can hold more water. We usually notice it when it goes the other way: the air cools and has more water vapor than it can hold. Some of the water vapor condenses into water droplets. If the droplets land on something, we call it ″dew″. If it is high in the sky, we call the droplets ″a cloud″. If it is near the ground, we call it ″fog″.

Chapter 4

The Piston Engine

Most cars, airplanes, and chainsaws get their power from burning hydrocarbons in a combustion chamber. We say they have *internal combustion engines*. There are many types of internal combustion engines: jet engines, rotary engines, diesel engines, and more. In this chapter, we are going to explain how one type, piston engines, work. Most cars have piston engines.

Most piston engines burn gasoline, which is a blend of liquid hydrocarbons. Hydrocarbons are molecules made of hydrogen and carbon (and maybe a little oxygen). In the presence of oxygen and heat, hydrocarbons burn — the carbon combines with oxygen to become CO_2, and the hydrogen combines with oxygen to become H_2O. In the process, heat is released, which causes the gases in the cylinder to create a lot of pressure on the piston.

4.1 Parts of the Engine

The engine block is a big hunk of metal. There are cylindrical holes bored into the engine block. A piston can slide up and down the cylinder. There are two valves in the wall of the cylinder:

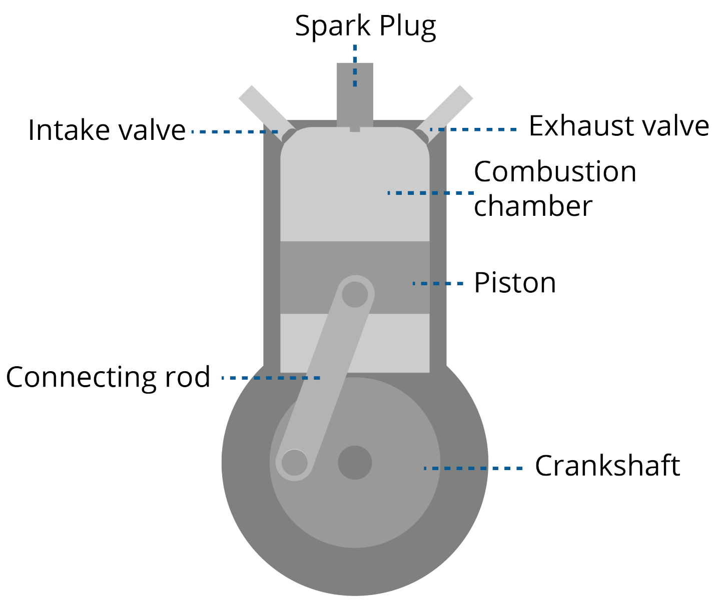
- Before the burn, one valve opens to let ethanol and air into the cylinder.
- After the burn, the other valve opens to let the exhaust out.

There is also a spark plug, which creates the spark that triggers the burn.

As you give the engine more gas, the cylinder does more frequent burns. When the engine is just idling, the cylinder fires about 9 times per second. When you depress the gas pedal all the way down, it is more like 40 times per second.

The cylinder has a rod that connects it to the crank shaft. As the pistons move back and forth, the crank shaft turns around and around. Sometimes a piston is pushing the crankshaft, and sometimes the crank shaft is pushing or pulling the piston. All the cylinders share one crank shaft.

How many cylinders does a car have? Nearly all car models have between 3 and 8 cylinders. The opening of the valve and the firing of the spark plugs are timed so that cylinders all do their burns at different times. This makes the total power delivered to the crank shaft smoother.

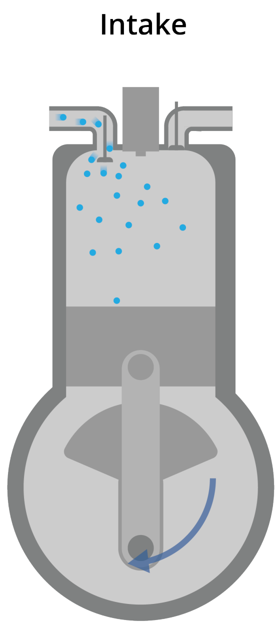


4.2 The Four-Stroke Process

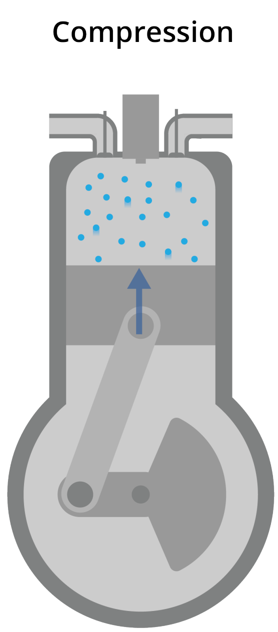
Cars have four-stroke engines — this means for every two rotations of the crank shaft, each cylinder fires once. Smaller engines, like those in chainsaws, are often two-stroke engines — every cylinder fires every time the crank shaft rotates. For now, let's focus on four-stroke engines.

Here is the cycle of a single cylinder:

- As the drive shaft turns, it pulls the piston down. The intake valve opens and lets the gas/air mixture into the combustion chamber.

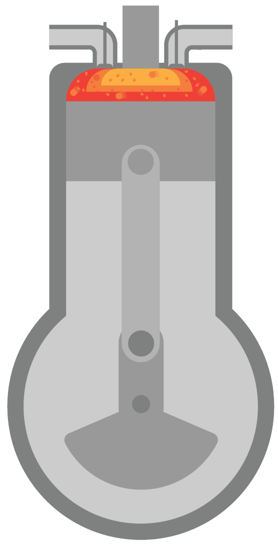


- As the piston reaches the bottom of the stroke, the intake valve closes.
- Now, the crank shaft starts to push the piston up, compressing the gas and oxygen.



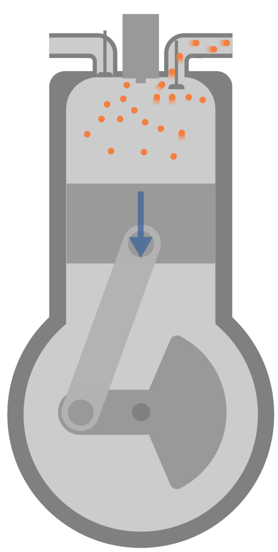
- As the piston reaches the top of its stroke, the spark plug creates a spark. The fuel and oxygen burn quickly. The cool liquid fuel becomes hot carbon dioxide and water vapor.

Combustion



- There is now very high pressure inside the cylinder. It pushes hard on the piston, which pushes the crank shaft.
- When the piston reaches the bottom of this stroke, the exhaust valve opens.
- As the crank shaft pushes the piston up, the carbon dioxide and water vapor is pushed out.

Exhaust



- When the piston reaches the top of this stroke, the exhaust valve is closed.

4.3 Dealing with Heat

Burning fuel inside a block of metal generates a large amount of heat. If there is too much heat, parts of the engine will start to melt. So, modern car engines are liquid cooled — there are arteries in the engine block carrying a liquid (called ”coolant”). The hot coolant is pumped through the radiator (where the air passing through takes away the heat), then back into the engine.

Note that the heat that is carried away by the coolant is wasted energy. In fact, of the total energy created in burning the fuel, most car engines only transfer about 30% to turning the crank shaft. About 35% of the heat goes out with the exhaust. About 30% is carried away by the coolant. The remaining waste (usually about 5%) is lost to friction.

4.4 Dealing with Friction

From the description, it is clear that there is a great deal of metal sliding against metal, which would grind the engine up quickly if there were no lubrication. In a modern car, the moving parts in the engine are constantly bathed in oil. There is an oil pump that causes it to get sprayed on the crankshaft, the connecting rod, and in the cylinder under the piston (that is, not on the combustion side).

The oil eventually falls through the oil into a pan at the bottom of the engine. The oil pump sucks the oil up, pushes it through a filter (so bits of metal are not pumped back into the engine), and is then sprayed on the moving parts again.

4.5 Challenges

With a piston engine, there are a lot of things that can go wrong. Let’s enumerate a few:

- *The seal around the piston leaks*. Mechanics say ”We aren’t getting any compression.” The cylinder doesn’t get much power to the drive train.
- *The valves open or the spark plug fires at the wrong time.* This is known as a timing problem.
- *The spark plug doesn’t make a spark*. The spark plug has two prongs of metal and electrons jump from one to the other. For a good spark, the prongs need to be a very precise distance apart. Sometimes you need to bend one of the prongs to get the right gap. This is known as *gapping*.

- *The mix of fuel and oxygen is wrong.* If there is too much fuel and not enough oxygen (so not all the fuel burns), we say the mix is too rich. If there is not enough fuel (so the pressure created by the burn is as high as possible), we say the mix is too lean.

4.6 How We Measure Engines

If you look up the specs on an engine, you will see the following:

- The number of cylinders
- The cylinder bore, which is the diameter of the cylinder
- The piston stroke, which is the distance the piston travels in the cylinder
- The compression ratio, which is the ratio between the maximum volume of the combustion change and the minimum volume of the combustion chamber
- What fuel it runs on

The difference between the minimum and maximum value of the cylinder is known as its *displacement*. The displacement represents the volume of air/fuel sucked into the intake valve before the compression begins.

We often talk about the displacement of the entire engine, which the cylinder's displacement times the number of cylinders. The displacement of an engine can give you a good idea of how much power it can produce.

For motorcycles, the displacement is often part of the name. For example, the Kawasaki Ninja 650 has about 650 cubic centimeters of displacement.

4.7 The Ford Model T and Ethanol

The Ford Model T was the first mass-produced car. It came out in 1908 and remained in production until 1927. It had a four-cylinder engine that would run on ethanol, benzene, or kerosene. For the purposes of this exercise, let's assume you are running yours on ethanol.

A molecule of ethanol has 2 carbon atoms, 6 hydrogen atoms, and 1 oxygen atom. The oxygen in the atmosphere is O_2. When one molecule of ethanol combines with 3 molecules of O_2, 2 molecules of CO_2 and 3 molecules of H_2O are created. A large amount of heat is also created — 1330 kilojoules for every mole of ethanol burned.

The engine block is usually very hot once the engine has been running. That is important because the ethanol will be completely vaporized at that temperature.

In any sample of air, 21 percent of the molecules will be O_2.

Exercise 8 Fuel Mix for the Model T

Working Space

On the Model T, a carburetor mixed the fuel and air before it went into the cylinder. The question to answer in this exercise is: How rich should the mix be at sea level (100 kPa)?

On the Wikipedia page for the Model T, we see the following facts:

- Cylinder bore: 9.525 cm
- Piston stroke: 10.16 cm

You can assume that the air/fuel mixture is 80° C before the pre-burn compression starts. (Thus, the ethanol, which boils at 78° C, is in its vapor phase.)

The questions, then, are:

- What is the displacement of a single cylinder?
- How many moles of gas (80° C and 100 kPa) will get sucked through the intake valve?
- How many moles of vaporized ethanol should be part of that?
- How many moles of CO_2 and H_2O are created in each burn?
- How much heat is created in each burn?

(This exercise has a lot of steps, but nothing you don't already know. You will need the ideal gas law to figure out how much many moles of air gets dragged into the cylinder.)

Answer on Page 47

4.8 Compression Ratio

Most of the inefficiency of a motor is heat that escapes through the exhaust valve. If your piston stroke were long enough, you could keep increasing the volume (which would cool the gases inside) until the gases inside were the same temperature as the outside world. Then there would be no wasted heat in the exhaust.

For this reason, generally, engines with a higher compression ratios tend to waste less energy through the heat of the exhaust. The Model T had a compression ratio close to 4:1. Modern car engines typically have compression ratios between to 8:1 and 12:1.

Cars with especially high compression ratios often require fuels with a lot of kilojoules per mole — we say *high octane*. If the fuel does not have enough energy, the engine makes loud knocking noises, as the pistons do not have enough energy to push through their entire stroke.

It turned out that an easy way to boost the octane of the gasoline was to add a chemical called tetraethyl lead. Gasoline containing tetraethyl lead was known at "Leaded Gasoline", and was intended to prevent the knocking. It is difficult to overstate the damages caused by putting large amounts of lead in the air. Gradually, starting with Japan in 1986, every country in the world has banned leaded gasoline.

4.9 The Choke and Direct Fuel Injection

Most cars built before 1990 will have a carburetor, which ensures that the ratio between fuel and oxygen is constant, regardless of the amount of fuel released by the throttle.

If you go to start an old car on a cold morning, the cold engine will not vaporize the fuel properly, and the engine may not have enough power to start. For this reason, most carburetors have a *choke value* that makes the mix richer. (If you pull the choke valve, be sure to push it back after the engine warms up.)

The carburetor was a common source of engine problems and inefficiencies. Starting in the 1990s, car engines started using direct fuel injection. Air still came in through the intake manifold, but fuel was sprayed directly into the cylinder by a fuel injection system.

In modern cars, the fuel injection system is controlled by a computer (an *Engine Control Module* or ECM), which delivers the fuel at the perfect time with the perfect amount based on environmental variables like the temperature of the engine and the barometric pressure (usually related to that altitude at which the engine is operating).

Appendix A

Answers to Exercises

Answer to Exercise 2 (on page 9)

First, we convert the temperatures into Kelvin:

- Dawn: $12 + 273.15 = 285.15$
- Noon: $28 + 273.15 = 301.15$

So, the temperature T has increased by a factor of $\frac{301.15}{285.15} \approx 1.056$.

Thus, the volume of the air mattress has also increased by a factor of 1.056.

This means that the air mattress that had a volume of 1000 liters at dawn will have a volume 1056 liters at noon.

Answer to Exercise 2 (on page 9)

What is the pressure in kPA?

- Before squeezing: 100 kPa
- While squeezing: 120 kPa

So, the pressure P has increased by a factor of $\frac{120}{100} = 1.2$

$1/1.2 \approx 0.833$

The air in the bottle had a volume of 1 liter before squeezing, so it has a volume of 833 milliliters while being squeezed.

Answer to Exercise 3 (on page 10)

First, let's convert the known values to the right unit:

- Radius = 0.12 m
- Length = 0.5 m
- $T = 20 + 273.15 = 293.15$ degrees Kelvin
- $P = 600$ kPa $= 600,000$ Pa

The volume of the cylindrical chamber is $V = \pi r^2 h = \pi(0.12)^2 0(0.5) \approx 0.0226$.

The Ideal Gas Law tell us that $PV = nRT$. We are solving for n.

$$n = \frac{PV}{RT} = \frac{(600,000)(0.0226)}{(8.31446)(293.15)} \approx 5.68 \text{ moles of } O_2$$

Answer to Exercise 4 (on page 14)

$E = C_{V,m}(3 \text{ moles })(20 degreesCelsius) = (12.47)(3)(20) = 748$ Joules

$E = C_{V,m}(3 \text{ moles })(20 degreesCelsius) = (20.8)(3)(20) = 1247$ Joules

Answer to Exercise 5 (on page 16)

10 degrees Celsius is 283.15 degrees Kelvin. 30 degrees Celsius is 303.15.

For any gas:

$$E_K = C_{V,m} nT$$

And $C_{V,m} = 12.47$ for all monoatomic gases.

So, the energy at 10 degrees Celsius:

$$E_1 = (12.47)(3)(283.15) = 10,594 \text{ Joules}$$

The energy at 30 degrees Celsius:

$$E_2 = (12.47)(3)(303.15) = 11,342 \text{ Joules}$$

The difference?

$$E_2 - E_1 = 11,342 - 10,594 = 748 \text{ Joules}$$

Which is consistent with your earlier exercise.

Answer to Exercise 6 (on page 30)

When one mole of water goes from 33° to 17°, it will give off $(75.38)(33-17) = 1,206$ Joules or 1.206 kJ.

Tom needs 300,000 kJ, so he needs $300,000/1.206 = 248,739.72$ moles of water.

How many liters is that? $248,739.72 * 0.018 = 4,477.31$ liters.

How many barrels is that? $4,477.31/159 = 28.16$ barrels. He will need 29 barrels.

Answer to Exercise 7 (on page 31)

When one mole of mirabilite goes from 33° to 17°, it will give off $(550)(33-17)+82,000 = 90,800$ Joules or 90.8 kJ.

Tom needs 300,000 kJ, so he needs $300,000/90.8 = 3,304$ moles of mirabilite.

How many liters is that? $3,304 * 0.22 = 726.9$ liters.

How many barrels is that? $726.9/159 = 4.57$. He will need 5 barrels.

Answer to Exercise 8 (on page 42)

The pre-compression temperature is 80irc C $+273.15 = 353.15°$ K.

The radius of the cylinder is $9.535/2 = 4.7625$ cm.

The area of a cross section of the cylinder is $\pi r^2 = \pi(4.7625)^2 \approx 71.26$ ml.

So, the change in volume between the minimum and maximum volume is $(71.26)(10.16) = 724$ ml, or 0.724 liters.

(With four cylinders, the total displacement of a Model T is thus $(4)(724) = 2,896$ cc.)

Now we use the ideal gas to figure out how many moles of gas will fit into 0.724 liters at 100 kPa and 353.15° K.

$$n = \frac{PV}{rT} = \frac{(100)(0.724)}{(8.314)(353.15)} = 0.02466 \text{ moles of air+fuel}$$

So, if we suck n_a moles of air and n_e moles of vaporized ethanol in to the cylinder:

$$n_a + n_e = 0.02466$$

So

$$n_a = 0.02466 - n_e$$

21% of n_a is O_2:

$$n_{O_2} = 0.21 n_a = 0.21(0.02466 - n_e) = 0.005178 - 0.21 n_e$$

For a clean burn, we need 3 times as many O_2 molecules as ethanol molecules. Thus:

$$3n_e = n_{O_2} = 0.005178 - 0.21 n_e$$

Solving for n_e:

$$n_e = \frac{0.005178}{3.21} = 0.001613 \text{ moles of ethanol}$$

For every molecule of ethanol that burns we get 2 molecules of CO_2: 0.003226 moles.

For every molecule of ethanl that burns we get 3 molecules of H_2OI: 0.004839 moles.

How much heat? $(0.001613)(1330) = 2.145$ kilojoules from each burn.