Changing the Antifreeze Concentration

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Here's a problem that I came up against in getting our cars ready for the winter. During the summer, both of our cars needed coolant while on the road. We added water because an antifreeze mixture wasn't available. Thus, the starting mixture was 50% antifreeze, 50% water, but then water was added to dilute the mixture. Now I need to remove some of the coolant and refill with pure antifreeze to protect the cars over the winter. The problem addressed here is: how much coolant do I remove and replace with 100% antifreeze to get back to the desired 50% antifreeze mixture?

Most folks would probably just drain all of the antifreeze and replace it with a new mixture. But this had been done recently for both of these cars, so it made more sense to drain some coolant and replace it with pure antifreeze.

I also discuss the refractometer I used to make the measurements with.

Theory

The problem is not hard to solve, but if you're like me, you took your chemistry class a long time ago and are a bit fuzzy on the details. Here are the steps we'll follow.

First, we'll look at a graph (Figure 1 below) that represents the freezing point of an ethylene glycol and water mix as a function of the weight fraction of ethylene glycol (the antifreeze I was using contains ethylene glycol). This graph is needed because we measure the freezing point of the coolant with a refractometer. We use the graph to translate this measurement to an ethylene glycol dilution with water.

> The wikipedia page used for Figure 1 is out-of-date and no longer contains the indicated data. Instead, you can go to https://www.engineeringtoolbox.com/ethylene-glycol-d_146.html for reference information.

Once we decide what temperature protection we want for the car, we also use the graph to translate this to the target ethylene glycol dilution we want to wind up with.

Then we assume we know the volume V_d of coolant we remove and replace with pure ethylene glycol. We'll derive an equation relating the following variables and solve for V_d .

The symbols we use are:

V = volume of coolant system
V_d = volume of existing coolant to remove and replace with 100% antifreeze
C_0 = original volume concentration of antifreeze
C = final target volume percentage concentration of antifreeze

The density of ethylene glycol is 1.113, or about 11% greater than water. Since this is pretty close to water, I'm going to make the assumption that **the weight fraction of the mixture is about the same as the volume fraction of the mixture** (because the graph in Figure 1 below is in terms of weight fraction). This will be close enough for what I'm doing and I can always make a small correction after the initial attempt at correction. I'm using ethylene glycol; since propylene glycol's density is much closer to water, this is an even better approximation for propylene glycol.

Let's look a bit more closely at volume concentration. This ranges from 0 to 1. If you have a 0.2 volume concentration of a solution of something, it means you have 0.2 volume units of solute for every 0.8 volume units of solvent. Contrast this to mass density measured in mass per unit volume. Both are useful. The volume concentration approach is easiest to use when you're

dealing with liquids. The mass concentration is handy when you're measuring the mass of solids and dissolving them in a solvent. In the following, "concentration" will mean volume concentration unless otherwise stated. You'll often see the volume concentration fraction expressed as a percentage.

Here's the relationship between the freezing point and volume fraction concentration for ethylene glycol (from https://www.engineeringtoolbox.com/ethylene-glycol-d_146.html):
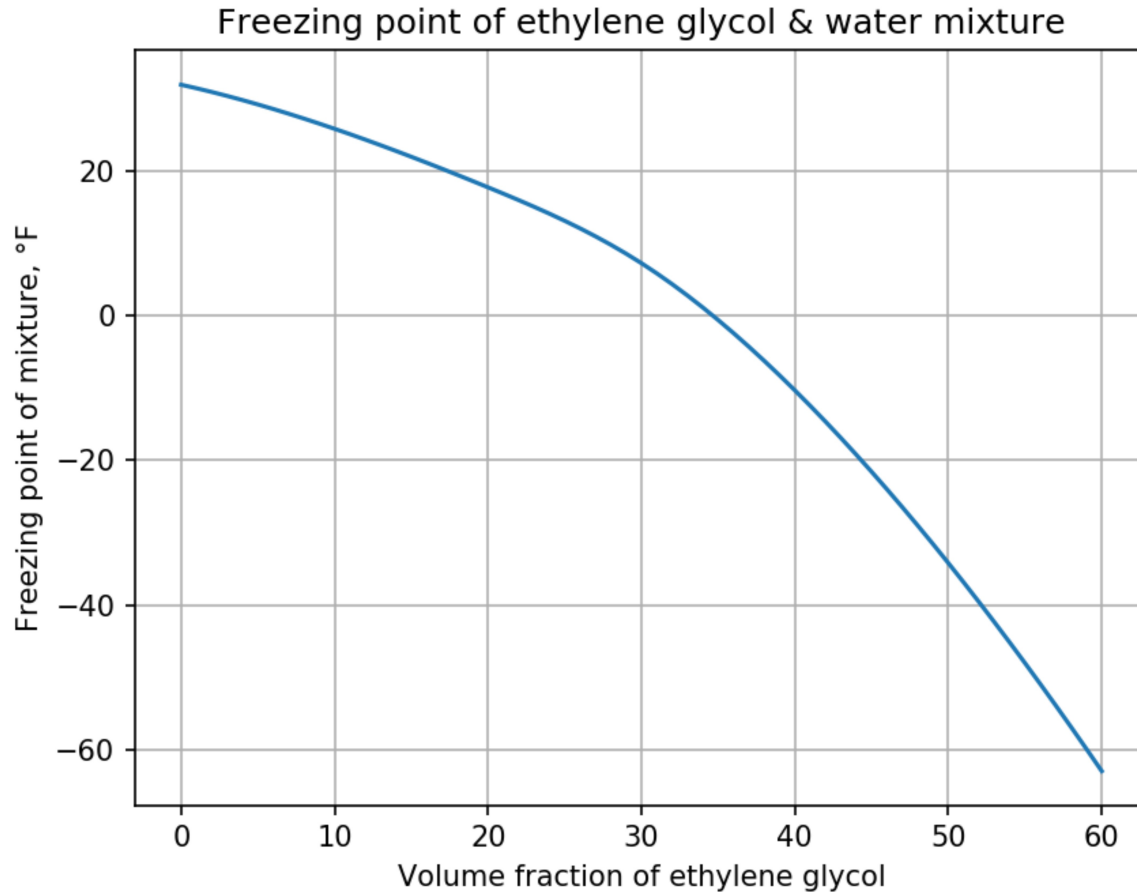
Figure 1

Dilution problem 1

First, let's look at the typical dilution problem -- it's not the problem we want to solve, but it might be useful to you in other problems. Suppose we have a volume V_0 of a solution that has a volume concentration of C_0 (C_0 will be a fraction between 0 and 1). What is the resulting volume concentration if we add a volume V of pure solvent? The new volume V_{new} will be $V + V_0$ and the new volume concentration will be lower than the original volume concentration. We haven't changed the mass of the dissolved material (solute), of which we had a volume of C_0V_0 prior to dilution. Thus, the new volume concentration will be

$$C = \frac{C_0 V_0}{V_{new}} = C_0 \frac{V_0}{V + V_0} = C_0 \left(\frac{1}{1 + \frac{V}{V_0}} \right)$$

or

$$\frac{C_0}{C} = 1 + \frac{V}{V_0}$$

(1)

Does this make sense? If we add $V = 0$ of solvent, the new volume concentration is the same as the old. If we add $V = V_0$, then the new volume concentration is half of the old. If we add a very large amount of solvent, then the new volume concentration C approaches zero. Since $V \geq 0$, we always will have that C_0/C will be greater than 1, or $C \leq C_0$. Thus, the formula makes sense at the boundaries.

There are liquids that when mixed together, the total volume isn't the sum of the individual volumes (an example is ethanol and water). Note I make the assumption that this doesn't happen here with antifreeze and water; the assumption was borne out by the derived formulas working adequately. Even if this does happen, the formulas are approximately correct for very dilute solutions.

Dilution problem 2

The above problem easily generalizes to the case of adding together two amounts of two different dilutions to get a third resultant solution. Suppose we have volume V_1 with concentration C_1 and volume V_2 with concentration C_2. When we mix them together, what's the concentration of the resultant mixture? The final volume will be V and the final concentration will be C. We thus have

$$C = \frac{C_1 V_1 + C_2 V_2}{V} = \frac{C_1 V_1 + C_2 V_2}{V_1 + V_2}$$

(2)

You can remember this equation as $CV = C_1 V_1 + C_2 V_2$. There are five variables, so if you know four of them, you can solve for the unknown.

Original problem

Now let's solve the original problem. I want to start with a volume V, remove a discard volume V_d, then add in a volume V_d of pure antifreeze to make the new volume V again. The original volume concentration is C_0 and the desired new volume concentration is C.

Start by assuming we know V_d. Thus, we start with a volume $V_0 = V - V_d$ of antifreeze/water mixture at a volume concentration of C_0. The original amount of pure antifreeze is $C_0 V_0$. Then we add V_d of pure antifreeze to get a final volume of V. Thus, the final volume concentration (as a fraction between 0 and 1) will be

$$C = \frac{(\text{original amount of pure antifreeze}) + (\text{new amount of pure antifreeze})}{V} = \frac{C_0(V - V_d) + V_d}{V}$$

Since we know C_0 (we measure it) and we've picked the C we want, then we solve for V_d to get

$$\boxed{V_d = V \frac{C - C_0}{1 - C_0}}$$

(3)

Let's check that this makes sense. First, we'll agree that $C \geq C_0$ in order to keep the numerator positive (i.e., we want the final concentration of ethylene glycol to be larger than the original concentration). If $C = C_0$, then $V_d = 0$, as we'd expect. If we want $C = 1$, then $V_d = V$, meaning we'd have to replace all of the coolant. Thus, things make sense at the boundaries.

We could also have written down the solution to this problem by substituting the proper terms in the formula in the previous section.

Examples

Example 1: 1984 Suburban

For one of our cars, the capacity of the cooling system is 16.6 liters. I want to have approximately a 50% antifreeze mixture. I used a refractometer (see the next section for details) to measure that the freezing temperature of the antifreeze mixture was +5 °F. Using the graph (Figure 1 above), this means the starting antifreeze concentration was 0.21. How much existing antifreeze do I have to remove and replace with 100% antifreeze to make the new antifreeze solution a 50% concentration? The numbers are

$C = 0.5$
$C_0 = 0.21$
$V = 16.6$ liters

which result in

$$V_d = V\frac{C-C_0}{1-C_0} = 16.6\frac{0.5-0.21}{1-0.21} = 16.6\frac{0.29}{0.79} = 6.1 \text{ liters}$$

This is slightly over 1.5 gallons (in the US, antifreeze is sold typically in 1 gallon containers).

This result can be tested by dealing first with a small volume of original coolant. Start with a volume of 1 unit, withdraw 0.367 of a volume unit, then add back in 0.367 of a volume unit of pure antifreeze. The new solution should have a percentage concentration of 50%.

Check

I withdrew 10 ml of the radiator antifreeze solution with a syringe and put it into a container.   As it was 34 °F outside, I let the refractometer and solution sit in the kitchen for an hour and a half. Then I tested the solution and it once again measured a freezing point of 18 °F, duplicating the previous measurement. I then withdrew 3.7 ml of antifreeze solution and replaced it with 3.7 ml of pure antifreeze solution. The new measured freezing point was -32 °F. The expected value was somewhere between -30 and -34 °F (depending on who you trust for the freezing point of a 50% solution), so this verified that the above formula worked.

The actual replacement worked fine.

Example 2: 1972 Nova

This example was done on 24 Nov 2018. My son and I have been working on his project car, a 1972 Nova. We installed a 4.8 liter Chevy LS1 engine in it that we got from a junkyard along with a new aluminum radiator.

When we charged the cooling system with antifreeze, we first added 1 gallon of ethylene glycol antifreeze. The engine had been run before with the radiator filled with water, so we first drained the radiator, but this of course left water in the block. We had to add roughly another 1.8 gallons of tap water to get the radiator fully filled and the air bubbles out of the system. The engine would overheat and shut down when we didn't have enough coolant and the air "burped" out of the system by squeezing the top radiator hose. I'd estimate we lost about 0.1 gallons while the radiator cap was off and we were watching the system burp itself after the engine was running with the cap off.   We put the cap back on and ran the system long enough to verify that the thermostat had opened and coolant was circulating through the system. I had measured the opening temperature of the thermostat by boiling it on the stove at about 190 °F.

A couple of days later I measured the freezing point of the radiator's coolant with a refractometer. It measured 3 °F.

I want to remove enough coolant and add pure ethylene glycol to get the protected temperature to -20 °F (the lowest temperature I remember in 40 years where I live). This is close enough to the

-35 °F of a 50:50 mixture that we'll just shoot for a final concentration of 0.5.

The starting variables are thus

> C- = 1/2.8 = 3.6
> V = 2.7 gallons
> C = 0.5

We use equation (3) to get how much liquid to remove before adding the pure ethylene glycol:

$$V_d = V\frac{C-C_0}{1-C_0} = (2.7 \text{ gal})\frac{0.5-0.36}{1-0.36} = 0.6 \text{ gal}$$

Since I used a 1 liter graduated cylinder to measure the volume removed, this volume in ml is 2300.

Refractometers

A refractometer is an optical tool that measures the index of refraction of a material. They stem from the original Abbe refractometer developed in the 1800's.

Here's an explanation of an Abbe refractometer from http://www2.ups.edu/faculty/hanson/labtechniques/refractometry/theory.htm . The author, John Hanson, kindly granted me permission to reproduce it here:

> *...the liquid sample is sandwiched into a thin layer between an illuminating prism and a refracting prism (Figure 2). The refracting prism is made of a glass with a high refractive index (e.g., 1.75) and the refractometer is designed to be used with samples having a refractive index smaller than that of the refracting prism. A light source is projected through the illuminating prism, the bottom surface of which is ground (i.e., roughened like a ground-glass joint), so each point on this surface can be thought of as generating light rays traveling in all directions. Inspection of Figure 2 shows that light traveling from point A to point B will have the largest angle of incidence (θ_i) and hence the largest possible angle of refraction (θ_r) for that sample. All other rays of light entering the refracting prism will have smaller θ_r and hence lie to the left of point C. Thus, a detector placed on the back side of the refracting prism would show a light region to the left and a dark region to the right.*
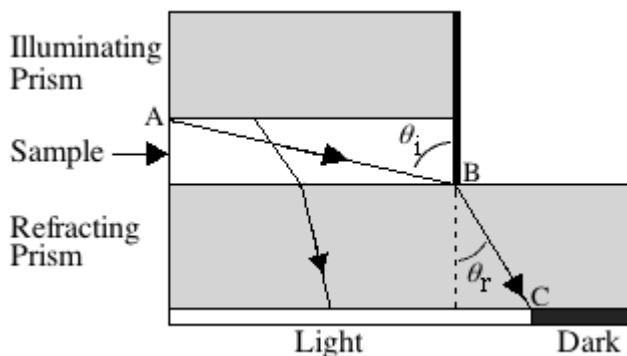
Figure 2. Cross section of part of the optical path of an Abbe refractometer. The sample thickness has been exaggerated for clarity.

> *As mentioned earlier, the speed of light in a substance is slower than in a vacuum since the light is being absorbed and re-emitted by the atoms in the sample. Since the density of a liquid usually decreases with temperature, it is not surprising that the speed of light in a liquid will normally increase as the temperature increases. Thus, **the index of refraction normally decreases as the temperature increases** for a liquid (Table 1). For many organic liquids the index of refraction decreases by approximately 0.0005 for every 1 °C increase in temperature. However for water the variation is only about -0.0001/°C.*

Note that the refractometer depends critically on the phenomenon of total internal reflection. This phenomenon is the progenitor of the dark to light line viewed in the refractometer. In the above figure, if the angle θ_i is greater than the critical angle, then the refracted ray BC is internally refracted and results in the dark region. The sine of the critical angle is the ratio of the indices of refraction of the sample and the refracting prism (and is only defined when this number less than 1). In order for the light to dark transition to be relatively sharp, the dimension AB has to be relatively small. Thus, though the hand-held refractometer appears to be a simple instrument, its design and implementation aren't trivial.

Misco 7084VP refractometer

I have a Misco 7084VP hand-held refractometer. You can get a Robinair 75240 Coolant and Battery Refractometer from Amazon for $42 as of 23 Nov 2009 and I've read some people have gotten the Misco 7084VP as low as $10 on ebay. If you get one, the first thing you should do is check it with distilled water -- the freezing point should be 32 °F or 0 °C.

> Update Nov 2018: Amazon's price is now $200 for one of these Misco 7084VP refractometers; the digital ones are about 50% higher. For that price, I'd suggest searching for "antifreeze refractometer" and finding a cheaper model; there are a number of them around $20 on Amazon (these are probably cheap Chinese knock-offs of the Misco design; note they don't include a built-in light source).

Beware of getting the older Misco models like the 7084VP that were red -- I've read on the web that these were less accurate than the newer orange-colored models.

Information on Misco:

> Misco Products Division
> 3401 Virginia Rd.
> Cleveland OH 44122
> (216) 831-1000
> website: http://www.misco.com

Here's a picture from the Misco website showing how these hand-held refractometers are constructed[1] (see http://www.misco.com/traditional.php):
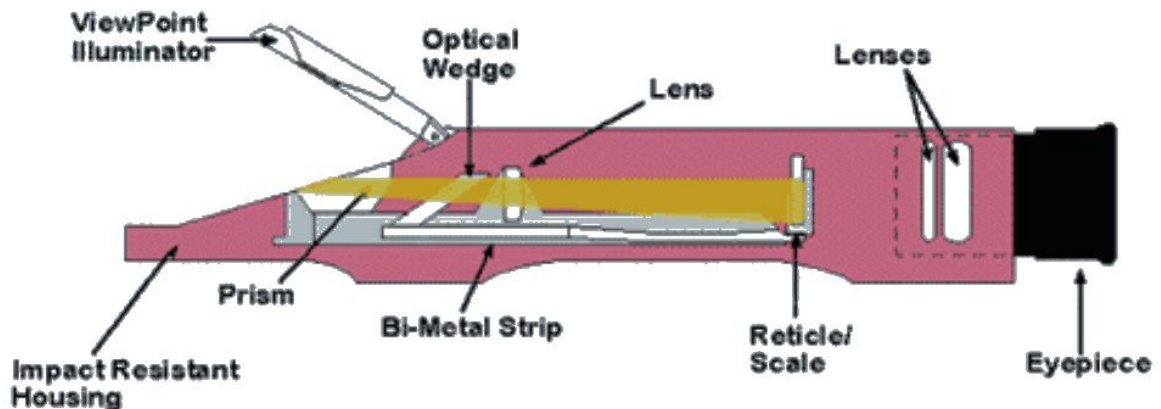
Because the index of refraction of a material is strongly dependent on temperature, the bimetallic strip is used to move the optical components to correct for temperature changes.

You may have not seen a refractometer before, so I'll show you some pictures. Here's the Misco refractometer from the side (photographed against a sheet of canary-colored paper):

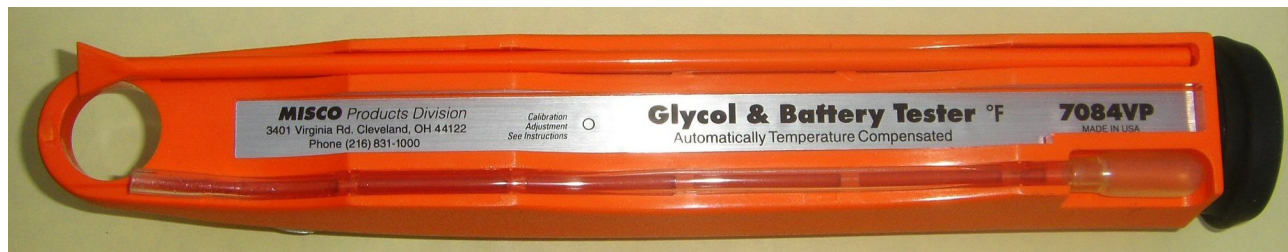1 Thanks to Misco for giving me permission to do this.

The hinged cover on the left covers the prism and contains a battery and an LED to provide illumination. Here's the cover lifted:

The attachments on the bottom are a dipping tool for batteries and a tube with a bulb that makes a flexible eyedropper to extract antifreeze samples:
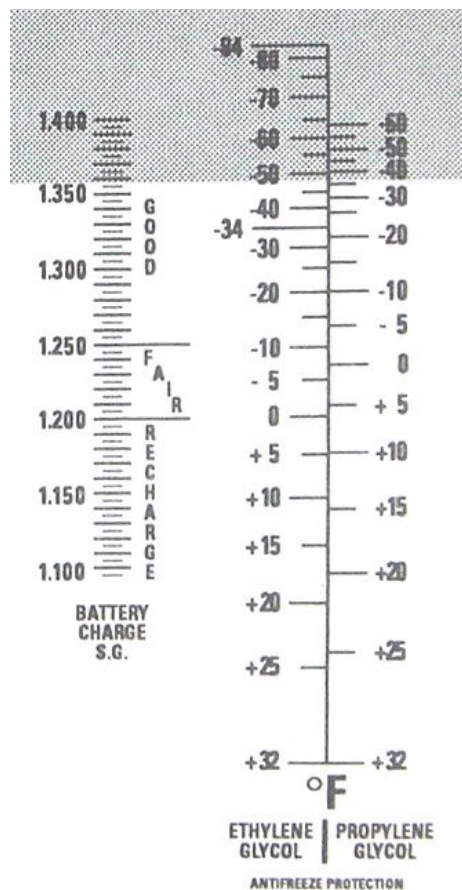

Here's a picture of what you see when you look through the eyepiece. It's fuzzy because it's a difficult picture to take (there's not a lot of light, leading to a long exposure time -- and I hand held the camera).
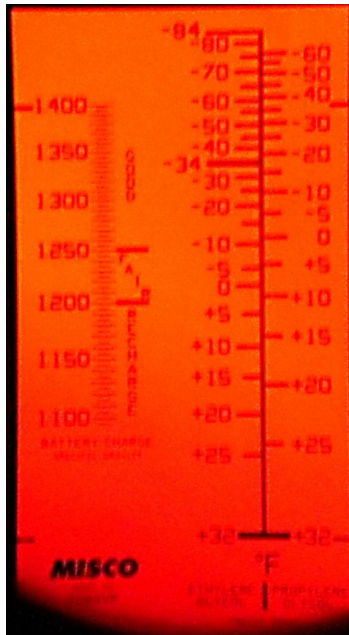
There are three vertical scales in view. The leftmost one is graduated in terms of the specific gravity of a lead-acid battery's electrolyte (i.e., sulfuric acid). This is used to tell you the charge state of the battery. The middle scale is the freezing point of an ethylene glycol and water solution. The right one is the same, but for propylene glycol. The refractometer is measuring the index of refraction of the liquid; this is directly related to the concentration of ethylene glycol, propylene glycol, or sulfuric acid, as the case may be. Here's a better image of the scales take from the manual:

-94
-80
-70
-60
-50

1.400

-60
-50
-40

1.350   G
           O   -40   -30
           O -34
           D   -30   -20
1.300
                  -20   -10
                             - 5
1.250   F
           A   -10
            I   - 5   0
1.200   R
           R   0   + 5
           E
           C   + 5   +10
1.150   H
           A   +10   +15
           R
           G   +15
1.100   E   +20
                  +20
BATTERY
CHARGE
S.G.   +25
                  +25

                  +32   +32
                    °F

ETHYLENE | PROPYLENE
GLYCOL | GLYCOL

ANTIFREEZE PROTECTION

To use the refractometer, you put a drop of liquid on the prism's surface after making sure the surface is clean. Aim the refractometer at some light or use the built-in LED in the cover to light the display. The display will show a light area separated from a dark area as in the previous figure. The line where these two areas meet is used as a cursor to read the number on the relevant scale. Thus, if we were reading the freezing point of an ethylene glycol mixture in the previous figure, we'd read -48 °F. It only takes a minute or so to figure out how to use one -- and since there are no moving parts, it's pretty foolproof. But as with all measurement equipment, you need to understand the principles of operation and not make dumb mistakes that cause you to get wrong numbers and make bad decisions from the data. It's an elegant measuring device. And I wish I had bought one decades ago, as it's the only tool you need to measure the concentrations of antifreeze and battery capacity.

A sensible thing to do is to make some calibration solutions to check the refractometer before use. Distilled water should give a reading of 32 °F (or 0 °C if yours reads in Centigrade). Make a 50-50 dilution of the pure ethylene glycol solution and it should read -34 °F.

I recommend that you don't store these calibration solutions in polyethylene containers, at least the 50% dilution solution. Polyethylene is permeable to water over a long period of time and the dilution level may change. Many folks are unaware of this, but I've seen it happen in 20-40 year-old fountain pen ink cartridges I purchased (and I've seen it happen on four or five different brands). Once-full cartridges can have 50% to 30% of their original contents (making you think the cartridge company stiffed you). An alternative is to mix a few drops of water and the same number of drops of pure antifreeze to make up a 50% solution when you need it.

After using the refractometer, it's good practice to wipe the prism with a clean cloth dipped in distilled water. Then it will be ready for service the next time you need it. With care and careful storage, your refractometer should outlast you (excluding the battery and LED).

For precise scientific work, the illumination for a refractometer is a monochromatic source, often the yellow sodium doublet (D line) at 589.0 and 589.6 nm. I remember setting up a lab on the Fabry-Perot interferometer when I was a student and being surprised that my eye could actually see a color difference between the fringes caused by these two sodium lines (they differ in wavelength by 0.1%). You have undoubtedly seen this illumination in sodium street lamps and in flames of a fire. For rough work like measuring the concentration of antifreeze, you can also make the measurement with a continuous spectrum like sunlight.

Calculating the concentration of sulfuric acid

The index of refraction of pure water at 20 °C is 1.333. We can derive an equation for the index of refraction of sulfuric acid as a function of the specific gravity of the acid, measured by the refractometer. For sulfuric acid at 18.3 °C (65 °F), the follow indices of refraction are given in the CRC Handbook of Chemistry and Physics, 59th ed., page E-357:

ρ = Density	n = Index of refraction for 589.3 nm
1.811	1.437
1.632	1.425
1.221	1.370
1.028	1.339

A quick regression in Open Office Calc shows that a reasonable equation for this relationship is

$$n = 1.335\,\rho^{0.13}$$

It is important, of course, to not use this equation to extrapolate. At the density 1.811, the equation is incorrect by 0.3%, so this is just for first approximations.

We can then relate the **density to the percentage of sulfuric acid** using the table on page F-7 in the CRC Handbook of Chemistry and Physics, 59th ed. A quick model was gotten to fit over the 0-60% sulfuric acid range:

$$\rho = 2.7 \times 10^{-5} p^2 + 0.00665\,p + 0.997$$

where p is the percentage of sulfuric acid and ρ is the density at 20 °C. The table above for density vs. index of refraction is for a temperature 1.7 °C less, so that's another source of error. Here's a plot of the data points and the curve:

Density of Sulfuric Acid

$$\rho = 2.7 \times 10^{-5} p^2 + 0.00665p + 0.997$$
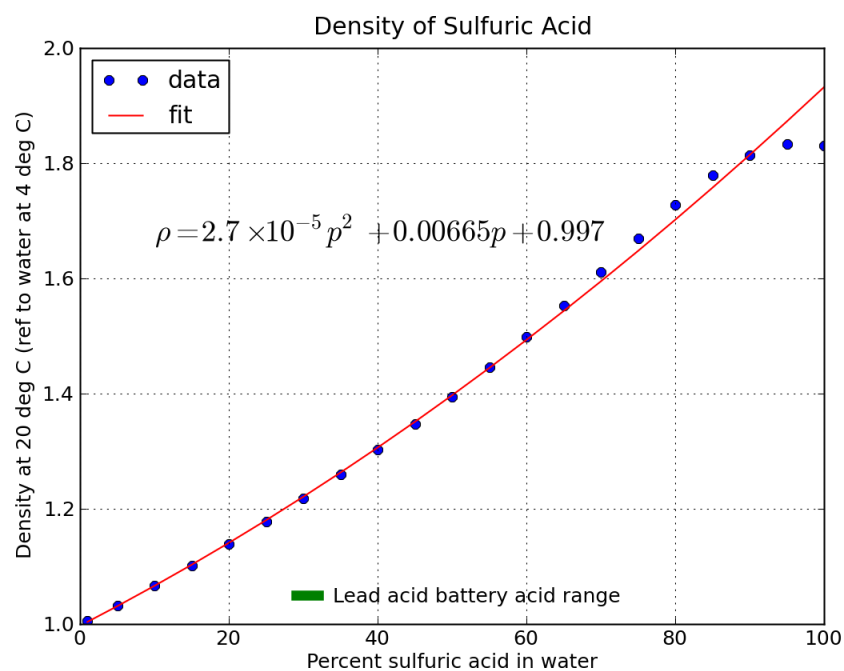
Here are the residuals in percent for this fitted curve f(p):

Residuals, %
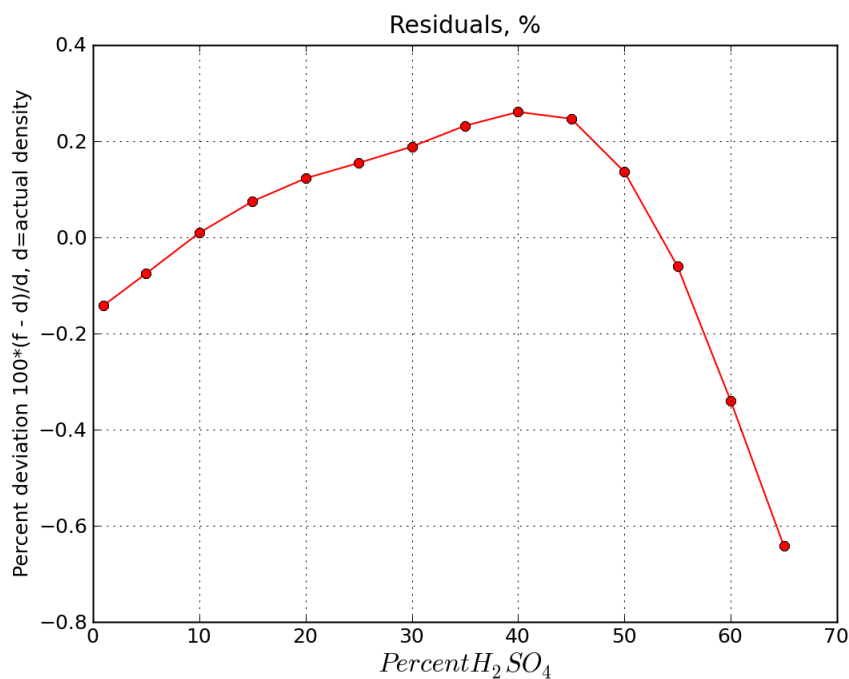
This model was not gotten by regression -- I simply fitted a linear equation by eye, then added in a quadratic term to make the fit a bit better.

For the usual applications in measuring lead-acid battery specific gravities, we can thus calculate the density within about half a percent.