# The Density of Water

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**Abstract**

The following experiment is a quantitative study of the density of water between 0 and 10 degrees Celsius. The data suggests that the density of water has a linear dependence with density even through the freezing point. Suspicions arise since the density of water is known to peak at around 4 degrees Celsius. Therefore, only qualitative analysis is performed and no conclusions are drawn.

**Introduction / Theory**

Given the widespread use and near universal access in industrialized nations, the physical characteristics of water has been the topic of much research in the physical sciences. Due to its popular use in calibrations, the density of water has come under great scrutiny in an effort to obtain accurate values.

With most liquids the density is proportional to the temperature of the liquid at constant pressure. The density of the liquid increases as the temperature drops through the freezing point, which is the point at which a liquid becomes a solid. This increase in density causes most solids to sink in their corresponding liquids.

This is not true of water. The crystalline structure of ice is less dense than liquid water. As water cools, the density increases until it peaks around 4 °C and drops off as the molecular make up of water changes. Hence, ice floats in cold water.

**The density of water vs temperature**

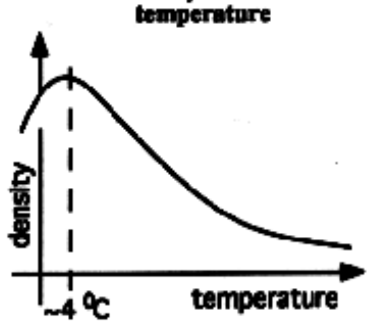


Figure 1: A plot of the expected density of water as it varies with temperature (C).

This change in density can be accurately measured by placing a constant amount of water in a vibrating glass tube. As the temperature of the water changes, the resonant frequency of the tube will also change. The changes in frequency can be calibrated to changes in water density. This allows a correlation between the changes in density and changes in temperature.

The resonate frequency, f is related to $\omega$ by: $\omega = 2\pi f$ where $\omega$ is related to the mass of the tube:

$$\omega = \sqrt{\frac{k}{m}} \qquad (1)$$

The frequency of vibration is linearly related to $m^{-1/2}$;

$$f \propto m^{-\frac{1}{2}} \qquad (2)$$

For a fixed volume, density is proportional to mass;

$$f^{-2} \propto m \propto \rho \qquad (3)$$

which gives a linear relationship between the density of the water in the tube and one over the frequency squared.

$$\rho = af^{-2} + b \qquad (4)$$

Where a is the slope and b is the y intercept. a and b must be experimentally determined before data analysis of density vs temperature can take place.

**Apparatus / Procedure**

In order to measure the density of water, the temperature of the water in the tube and the vibration of the tube must be accurately controlled and measured. The first portion of the experiment involves tube vibration and measurement and is performed by two instruments. The vibrating tube densimeter uses a glass tube which is filled with distilled water and sealed.

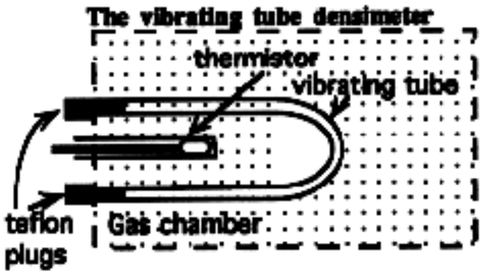


Figure 2: A diagram of the gas chamber within the DMA 602.

The Anton Paar DMA 602 densimeter vibrates the glass tube at its resonant frequency within a chamber of inert gas and sends the pulses of vibration to an HP 5385A Frequency counter. The HP 5385A takes rather sensitive readings which vary significantly over a given period of time. In order to offset this variation, the frequency counter is set to count the pulses over a 10 second period and average the number of pulses per second, thereby obtaining a more accurate representation of the resonant frequency.

In order to control the water temperature, A Lauda bath is used to circulate antifreeze around the chamber of inert gas thus regulating the temperature of the gas which in turn regulates the temperature of water in the tube. The temperature of the water is measured by a YSI thermistor which is placed in a glass tube positioned in the center of the gas chamber next to the vibrating tube.

The resistance of the thermistor is measured by a Keithley 199 multimeter. The multimeter uses a four terminal connection, where two wires supply current to the thermistor, and the other two measure the voltage thus determining the resistance.

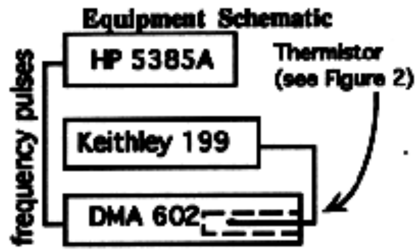


Figure 3: A schematic showing the wiring together of the instruments used in this experiment to collect temperature and frequency data.

Raw data was taken in the form of resistance and frequency. These values must be converted to temperature and density respectively. Fortunately, Dennis Kuhl[2] had already taken calibration data for thermistor resistances. Given that Kuhl experiment used the same YSI thermistor under much more controlled conditions, the data and curve fits he derived for the relation between temperature and resistance are used to calibrate our equipment.

Even though Kuhl[2] took calibration data which covered the range from 30 to -15 degrees Celsius, he never performed a curve fit on this region. He did include the following formula to convert the resistance values to temperature;[3]

$$T = \frac{1}{a + b(\ln R) + c(\ln R)^2 + d(\ln R)^3} \tag{5}$$

Given that Kuhl never performed a curve fit, values were not listed for the constants a, b, c, and d at low temperatures. Therefore, Igor was employed to perform a curve fit of Kuhl's data using equation 5. This formula had to be modified slightly for Igor to calculate the coefficients properly.

$$T = \frac{1}{a + b(\ln R) + c(\ln R)^2 + d(\ln R)^3} - f \tag{6}$$

The f coefficient has the same effect on the formula as the inverse of the a coefficient. However, in order for Igor to perform the curve fit with any kind of accuracy, we had to include this coefficient.

For the temperature range of 30 to -10 degrees Celsius, Igor determined the following coefficients for equation (6);

$a=3.49181*10^{-3}$ $d=-4.09868*10^{-6}$

$b=-5.55866*10^{-4}$ $f=144.347$

$c=4.11007*10^{-6}$

Which gives temperature in °C when R is in kΩ and produced the following curve fit:

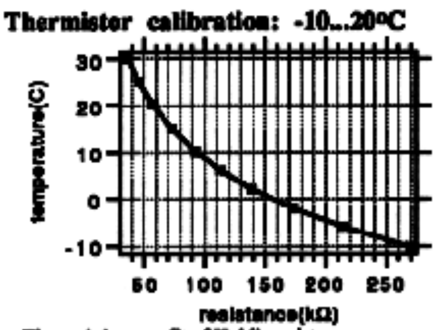


Figure 4:A curve fit of Kuhl's resistance and temperature values for the thermistor calibration.

Since the density to temperature relationship is relatively linear from 10 to 20 degrees, this region is used to calibrate the densimeter. Calibration data in the form of resistance vs. frequency is taken from 20 degrees to 10 degrees in 2 degree steps. The resistance is converted to temperature using equation (6). However, the frequency must be calibrated to density.

The CRC[1] was consulted to determine known values for density vs. temperature. The following is a plot of known temperature and their corresponding densities as taken from the CRC.

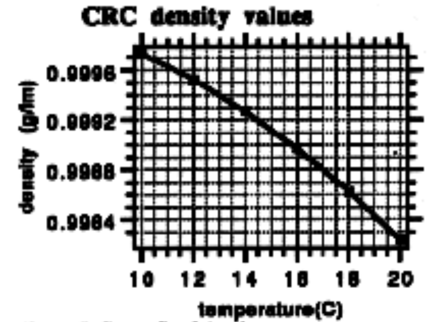


Figure 5: Curve fit of density vs temperature taken from the CRC for use in the densimeter calibration

The curve fit for density vs temperature is of the form:[2]

$$\rho_w = \frac{a + bT + cT^2 + dT^3 + fT^4}{1000*(1+gT)} \qquad (7)$$

This formula provides a relationship between temperature T and a corresponding density in $g/cm^3$. For the temperature range under investigation, the following coefficients were determined by Igor;

$a=997.409$ $d=3.40231*10^{-3}$

$b=32.3669$ $f=-5.97965*10^{-5}$

$c=-8.40458*10^{-2}$ $g=3.15835*10^{-2}$

Given that the calibration data was taken in the form of temperature and frequency, formula (7), with the above coefficients, was used to convert the temperatures to densities. This allowed us to plot density vs frequency.

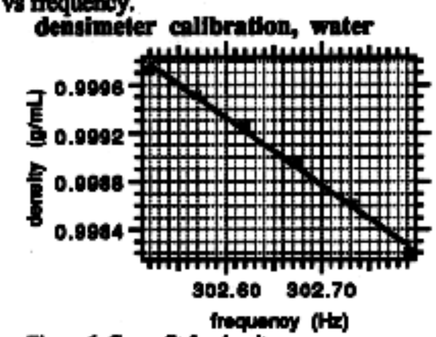


Figure 6: Curve fit for density vs frequency used to calibrate the DMA 602 densimeter

The curve fit for density vs frequency is of the form :[3]

$$\rho = \frac{a}{f^2} - b \qquad (8)$$

Where the coefficients for the region in question are as follows:

a=77323.6 b=-0.154876

The above relationship and coefficients were used to convert the resonant frequency of the tube to the density of water, in the actual data.

Once these formulas were derived, equations (6) and (8) are used to convert the resistance and resonant frequency collected in the actual data to temperature and density so that analysis may be performed.

## Results / Discussion

Data was taken for frequency and resistance from 10 to 0 degrees Celsius in one degree steps, and was then converted to density and temperature.

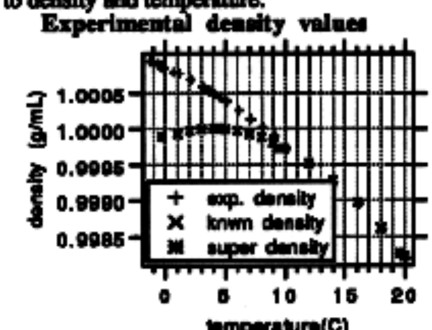


Figure 7: A comparison of experimental density values, known values taken from the CRC and densities of supercooled water.[4]
note: calibration data also included as the experimental density and temperature readings between 10 and 20 degrees Celsius.

For the values below 10 degrees Celsius, the density values diverged abruptly (see Fig. 7). The measured density continued to increase almost monotonically as the temperature dropped. This is disturbing since the known density of water peaks at 4°C. We even took the water below 0°C at the risk of cracking the tube. The density did seem to show signs of leveling off at the lower temperatures; however, it never quite peaked.

There are a few possibilities for the cause of this near monotonic trend. The curve fit for density vs frequency is linear while the density values have a slight curve to them. According to the theory explained by Linda King[3] in her thesis report on fluid density, there is a monotonic relationship between the density of the water in the tube and the inverse square of the tube's resonant frequency.

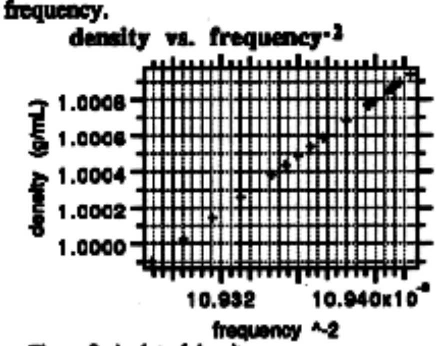


Figure 8: A plot of density vs. frequency$^{-2}$ lending evidence to the relationship in equation (8).

Given this relationship between the density and the inverse square of the frequency, there is also a monotonic relationship between the density and the frequency.[3]

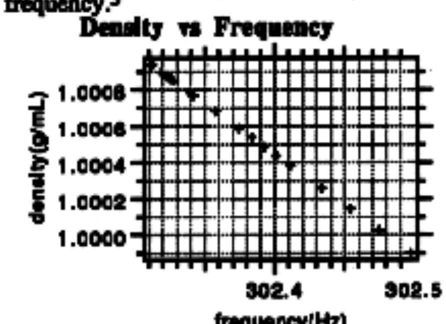


Figure 9: A plot showing the linear relationship between density and frequency.

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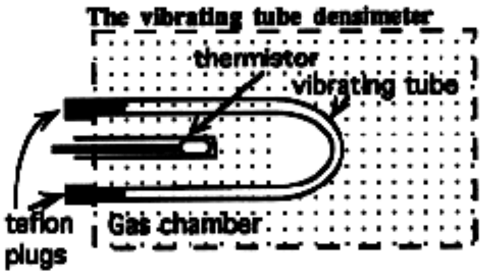


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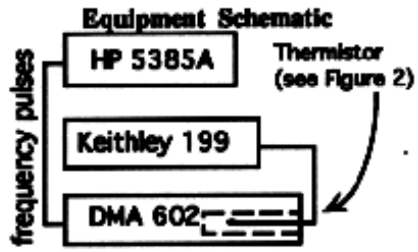


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The f coefficient has the same effect on the formula as the inverse of the a coefficient. However, in order for Igor to phenomenon, suggesting errors in either our thermistor calibration or our calculations.

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[1]Hodgemann, Charles D. Handbook of Chemistry and Physics, 31st edition; (Chemical Rubber Publishing Co. Cleveland OH 1953)

[2]Kuhl, Dennis E. The Excess Volume Effect of the Binary Liquid Mixture Perfluoromethylcyclohexane + Isopropyl Alcohol; (College of Wooster; Sr IS report; 1990)

[3]King, Linda D. An Investigation of the Excess Volume Effect of the Binary Fluid Mixture Perfluoromethylcyclohexane + Isopropyl Alcohol; (College of Wooster; Sr IS report; 1993)

[4]Hare, D.E. and Sorensen C.M. "Densities of supercooled $H_2O$ and $D_2O$ in 25m glass capillaries"; Journal of Chemical Physics 84, 9 (1986)

[5]G.S. Kell, Journal of Chemical Engineering Data 20, no.1,57 (1975)