

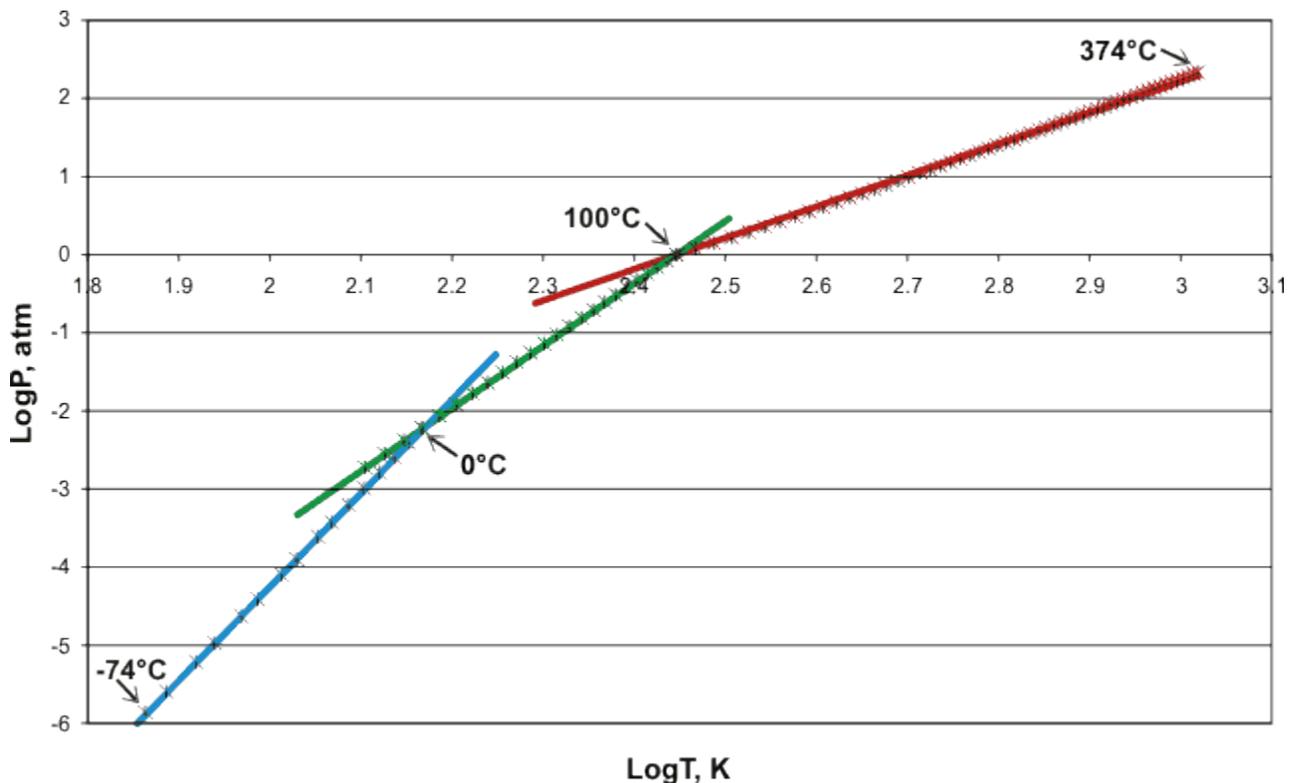
Water's Unexpected Properties

- ▼ Vapor pressure curves
- ▼ Pressure-density relationship
- ▼ Temperature-volume change relationship
- ▼ Temperature-viscosity relationship
- ▼ Temperature-enthalpy of vaporization relationship

There are several properties of water that do not constitute anomalies but are still remarkable. Until they are fully explained, they may be considered to be the result of coincidences. These unexplained properties will be described on this page.

Vapor pressure curves

There are many formulations giving the vapor pressure of ice^a and water over various temperature ranges, mostly involving many empirical parameters. However, the following approximate formulae are curious and give approximately straight-line Log-Log plots of integral gradients 12, 8 and 4 with only physically meaningful parameters. The points are experimental data [70]^b and the lines show the equations (T is the scaled temperature given in the power expressions, see later, and the LogT values have been shifted so that the LogP values show a continuous function).



The vapor pressure of ice is approximately given by the following relationship between pressure (atm) and temperature (K). T_0 is 126 K which is approximately the temperature for the phase change between glassy amorphous ice and deeply supercooled amorphous water (136 K; the glass transition temperature). Bpt and Mpt are the boiling point and melting points of water.

$$P = \left\{ \frac{T - T_0}{B_{pt} - (M_{pt} - T_0)} \right\}^{12}$$

The vapor pressure of water (-15 °C - 100 °C) is approximately given by the following relationship between pressure (atm) and temperature (K). T_1 is 162 K which is approximately the temperature for the phase change between glassy amorphous water and cubic ice (160 K).

$$P = \left\{ \frac{T - T_1}{B_{pt} - T_1} \right\}^8$$

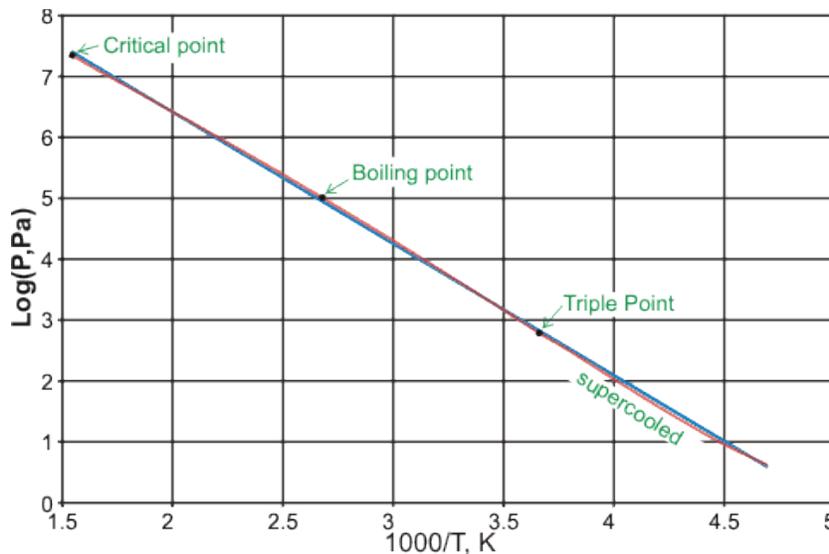
The vapor pressure of water (100 °C - 374 °C, Critical point) is approximately given by the following relationship between pressure (atm) and temperature (K).

$$P = \left\{ \frac{T - M_{pt}}{B_{pt} - M_{pt}} \right\}^4$$

These power laws not only obey the rule of thumb that candidate power laws should exhibit an approximately linear relationship on a log-log plot over at least two orders of magnitude in both the x and y axes [1769], but also contain the curious integral relationship between the exponents, both factors indicating that these relationships have a mechanistic physical cause.

I am grateful to Frank Grimer for pointing me at these relationships.

The proportionality between the logarithm of the vapor pressure and the reciprocal temperature for liquid water is near constant for its complete span from supercooled water through to the critical point, as shown below with data from [1802,1803]. The red line follows the experimental (or theoretical) data whereas the underlying blue line is the fitted straight line relationship.



[[Back to Top](#) ▲]

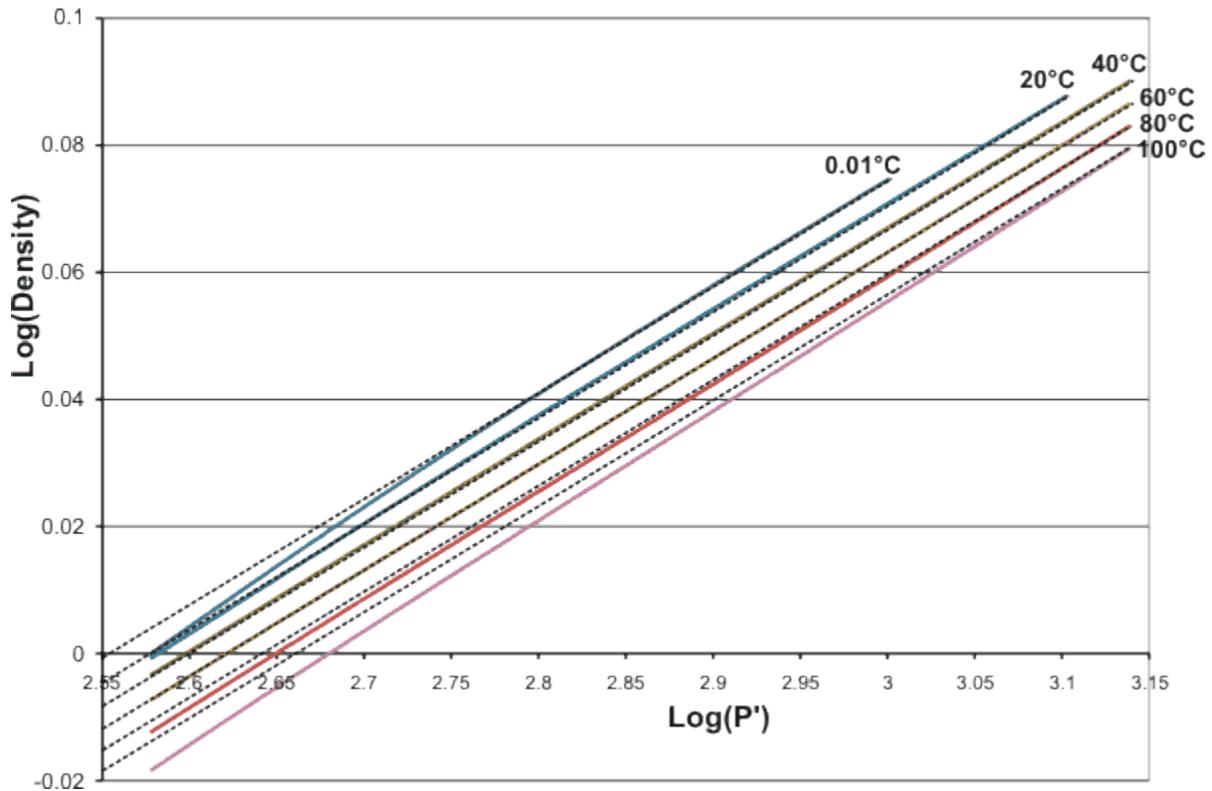
Pressure-density relationship

The density of liquid water tends towards an integral 6th power relationship with respect to pressure.

$$\frac{P + P_0}{T + T_0} = \rho^6$$

where P is the pressure (MPa), P₀ is 378 MPa, T is the temperature (K), T₀ is 85 K and ρ is the density (g/mL).

This relationship is shown below (P' is the scaled pressure, that is, the left side of the above expression) as the dashed lines, with the colored lines being the experimental data. The lines for 20 °C - 60 °C fit well but the power increases from 6 at lower and higher temperatures. The best fit is thus around the compressibility minimum at 46.5 °C. The extrapolated density at zero T and P is 1.28 g/mL which is close to the density for very high density amorphous ice (1.25 g/mL) with P₀ and T₀ being close to the conditions required for its formation.



As this power law does not obey the rule of thumb that candidate power laws should exhibit an approximately linear relationship on a log-log plot over at least two orders of magnitude in both the x and y axes [1769], it seems likely that this relationship is purely empirical.

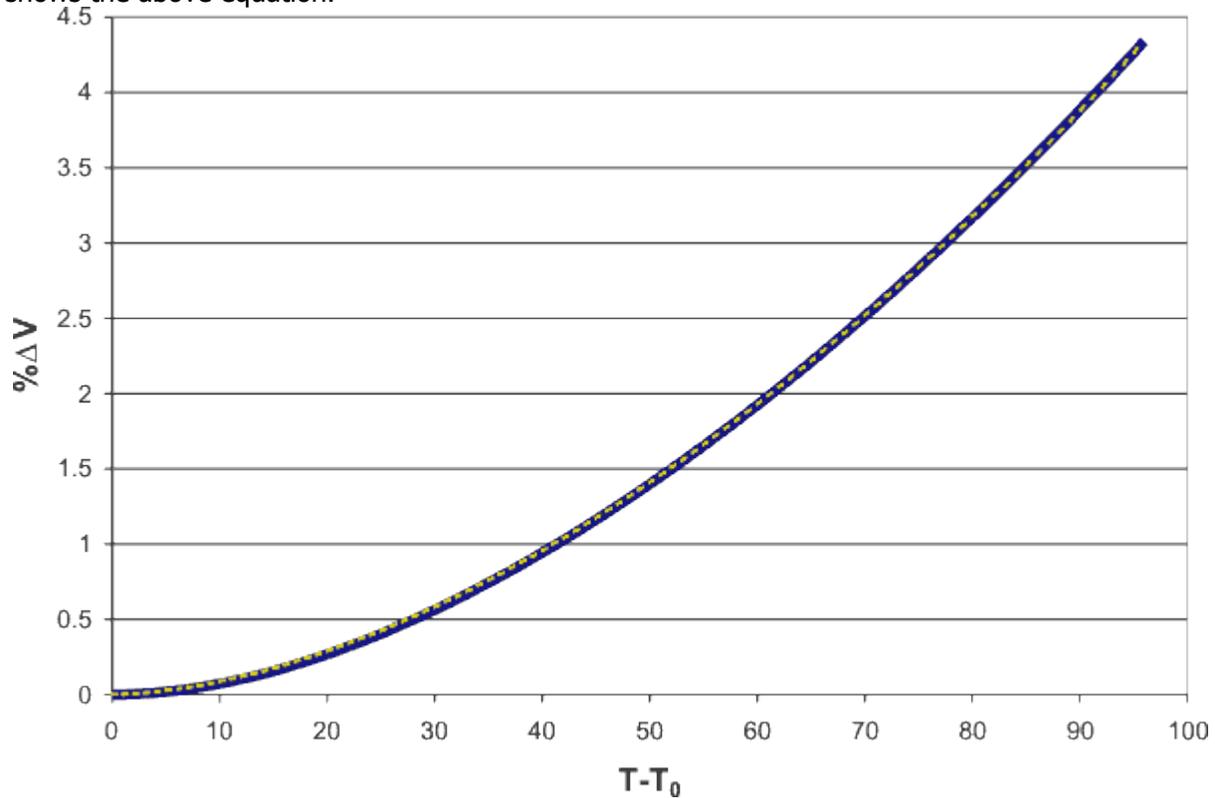
I am again grateful to Frank Grimer for pointing me at this relationship. [[Back to Top](#) ▲]

Temperature-volume change relationship

The incremental volume change increases as the square-root(3) power of the temperature above the temperature (T_0 , 3.984 °C) of minimum volume (V_0 , 1.00003 mL/g)

$$\frac{V - V_0}{V_0} = 0.272 \times \left(\frac{T - T_0}{T_0} \right)^{\sqrt{3}}$$

as shown below, where the solid blue line follows the experimental data and the dashed yellow line shows the above equation.

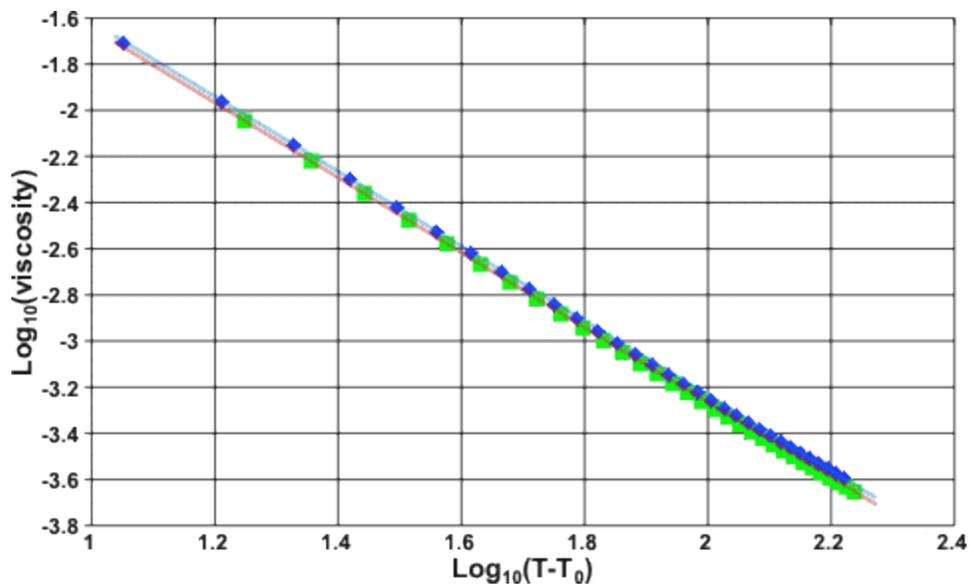


The square-root(3) term is related to the Vesica Pisces, being the ratio of the long to short diameter of intersecting expanded icosahedral water clusters (the short diameter being the distance between the centers of neighboring dodecahedra and the long diameter associated with a plane of water molecules between the two pentameric boxes (Figure 3h) joining them.

I am again grateful to Frank Grimer for showing me this relationship. [[Back to Top](#) ▲]

Temperature-viscosity relationship

The dynamic viscosity varies with the temperature above a baseline temperature, viscosity = $(T - T_0)^{1.637}$ for H₂O and viscosity = $(T - T_0)^{1.623}$ for D₂O; where T₀ = 225.4 for H₂O and 231.9 for D₂O, both these values being close to their respective homogeneous nucleation temperatures. The exponents are close to the golden mean, $(1 + \sqrt{5})/2$ (= 1.618).



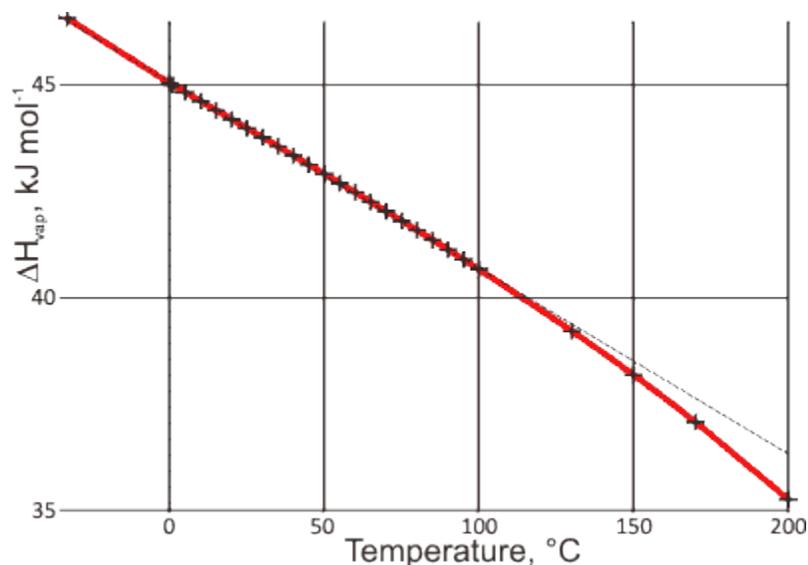
In the graph above, H₂O values are shown by green squares (red line) and D₂O values are shown by blue diamonds (blue line).

As this power law does not quite obey the rule of thumb that candidate power laws should exhibit an approximately linear relationship on a log-log plot over at least two orders of magnitude in both the x and y axes [1769], it seems possible that this relationship is curious but purely empirical.

Similar straight line graphs also exist for Log-Log relationships involving changes in diffusivity, isothermal compressibility and proton NMR relaxation with respect to temperature for liquid and supercooled liquid water [1886].

[\[Back to Top ▲\]](#)

Temperature-enthalpy of vaporization relationship



Remarkably the enthalpy of vaporization for liquid water reduces almost linearly with increasing temperature below 100 °C as the data graphed right demonstrates [906, 1934]. Note that fully

hydrogen bonded water molecules, in liquid water, must break two bonds per molecule to evaporate, so the average hydrogen bond energy given by this line is about 22.5 kJ mol^{-1} at $0 \text{ }^\circ\text{C}$.

This relationship has been described as showing the linear relationship of the hydrogen bond strength in water with temperature [1935]. At higher temperatures it is assumed that the greater loss of enthalpy with temperature is due to fewer hydrogen bonds per water molecule. This linear relationship is in general agreement with the quadratic relationship found with the hydrogen bond length of hexagonal ice with temperature over the range $-100 \text{ }^\circ\text{C}$ to $0 \text{ }^\circ\text{C}$ [1935], as bond length is thought approximately quadratically related to bond strength..

[Back to Top 

Footnotes

^a A discussion of the vapor pressure of ice over its entire range is available [1099]. [Back]

^b Details of the saturation vapor pressures of H_2O , D_2O , T_2O and their isotopic mixtures are given in [1790]. [Back]

Source:<http://www1.lsbu.ac.uk/water/strange.html>