

Explanation of the Thermodynamic Anomalies of Water (T1-T11)

- ▼ The heat of fusion of water with temperature exhibits a maximum at -17 °C
- ▼ Water has over twice the specific heat capacity of ice or steam
- ▼ The specific heat capacity (C_P and C_V) is unusually high
- ▼ The specific heat capacity C_P has a minimum at 36°
- ▼ The specific heat capacity (C_P) has a maximum at about -45 °C
- ▼ The specific heat capacity (C_P) has a minimum with respect to pressure
- ▼ The heat capacity (C_V) has a maximum
- ▼ High heat of vaporization
- ▼ High heat of sublimation
- ▼ High entropy of vaporization
- ▼ The thermal conductivity of water is high and rises to a maximum at about 130 °C

T1 The heat of fusion of water with temperature exhibits a maximum at -17 °C [15].

This strange behavior has been determined from the variation in ice and water specific heat capacities (C_p). It is due to changes in the structuring of supercooled water. As the temperature is lowered from 0 °C the hydrogen-bond strength of ice increases due to the reduction in their vibrational energy and this gives rise to an increasing difference (as temperature is lowered) between the enthalpy of the water and ice. At low temperatures (below about -17 °C) the continued shift, with lowering temperature, in the supercooled water $CS \rightleftharpoons ES$ equilibrium towards the ES structure reduces the enthalpy of the liquid water relative to the ice due to the consequent increase in hydrogen-bond strength and this causes the drop in the heat of fusion with lowering temperature. [[◀ Anomalies page : Back to Top ▲](#)]

T2 High specific heat capacity; C_V and C_P , $4.18 \text{ J g}^{-1} \text{ K}^{-1}$ at 25 °C (compare pentane $1.66 \text{ J g}^{-1} \text{ K}^{-1}$).

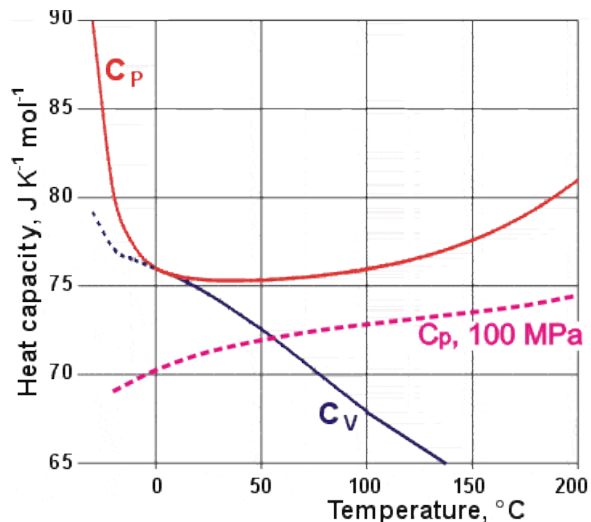
Water has the highest specific heat of all liquids except ammonia. As water is heated, the increased movement of water causes the hydrogen bonds to bend and break. As the energy absorbed in these processes is not available to increase the kinetic energy of the water, it takes considerable heat to raise water's temperature. Also, as water is a light molecule there are more molecules per gram, than most similar molecules, to absorb this energy. Heat absorbed is given out on cooling, so allowing water to act as a heat reservoir, buffering against changes in temperature. [[◀ Anomalies page : Back to Top ▲](#)]

T3 Water has about twice the specific heat capacity of ice or steam (compare benzene where $C_{P \text{ liquid}} = 1.03 \times C_{P \text{ solid}}$).

At its melting point the C_p s of ice-Ih and water are $38 \text{ J mol}^{-1} \text{ K}^{-1}$ and $76 \text{ J mol}^{-1} \text{ K}^{-1}$ respectively. The C_p s of the other ices may be up to about 40% higher (ice-three) than that of ice-1h but are all significantly lower than liquid water [606]. The specific heats of polar molecules do increase considerably on melting but water shows a particularly large increase [1723]. As water is heated, much of the energy is used to bend the hydrogen bonds; a factor not available in the solid or gaseous phase. This extra energy causes the specific heat to be greater in liquid water. The presence of this large specific heat offers strong support for the extensive nature of the hydrogen-bonded network of liquid water. [[◀ Anomalies page : Back to Top ▲](#)]

T4 The specific heat capacity (C_p) has a minimum at 36 °C.

It is usual for the specific heats of liquids to increase with increased temperature at all temperatures.



The C_v values for supercooled water may be erroneous, being calculated from other data and showing an apparent discontinuity at about -20 °C. An alternative extrapolation is available [1794].

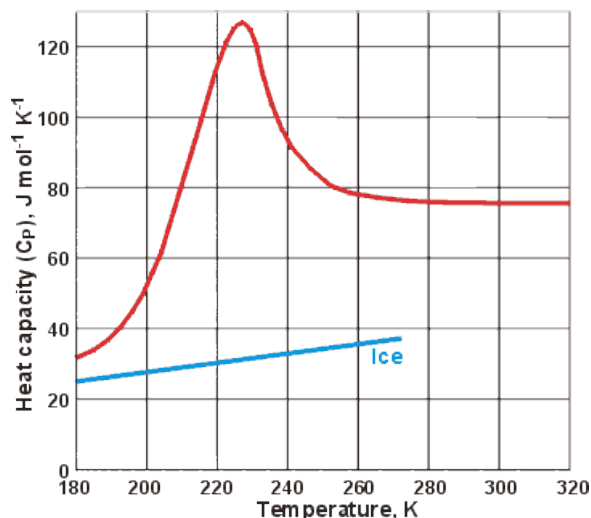
The (isobaric; also called isopiestic) specific heat capacity (C_p) has a shallow minimum at about 36 °C at 100 kPa ($D_2O \sim 120$ °C) with a particularly steep negative slope below 0 °C [15,67] (see right). It is interesting that this minimum is close to the body temperature of warm-blooded animals. The water cluster equilibrium shifts towards less structure (for example, CS) and higher enthalpy as the temperature is raised. C_p is the heat capacity at constant pressure defined by

$$C_p = (\delta H / \delta T)_p = T(\delta S / \delta T)_p \propto \langle (\Delta S)^2 \rangle_{TP} \propto \langle (\Delta H)^2 \rangle_{TPN}$$

(that is, equals change in enthalpy with temperature, and proportional to the square of the entropy (or enthalpy) fluctuations).^a The extra positive ΔH due to the shift in equilibrium (at low temperatures) as the temperature is raised causes a higher C_p than otherwise, particularly at supercooling temperatures where a much larger shift occurs [1353]. Note that generally thermal fluctuations ($\langle (\Delta S)^2 \rangle_{TP}$) increase with increasing temperature whereas the reverse is true of supercooled water. This addition to the C_p , as the temperature is lowered, is greater than the 'natural' fall expected, so causing a minimum to be created. Note that C_v equals C_p at the temperature of maximum density. Usually in liquids C_p is more than 20% greater than C_v .

As expected, the large specific heat changes with temperature at low temperatures is reduced at higher pressures and this specific heat-pressure minimum shifts to lower temperatures and disappears at high pressures (> 100 MPa, see above). The minimum in C_p has been associated with a discontinuity in the Raman depolarization ratio (that is, perpendicular/parallel polarization) data of degassed ultrapure water and hence a weak liquid-liquid phase transition at 34.6 °C (5.8 kPa) [1044]. [◀ Anomalies page : Back to Top ▶]

T5 The specific heat capacity (C_p) has a maximum at about $-45\text{ }^\circ\text{C}$.



There are large specific heat changes with temperature at low temperatures but deeply supercooled water has lower specific heat at very low temperatures. At sufficiently low temperature, there must be a maximum in the specific heat (C_p)-temperature relationship, so long as no phase change occurs. This maximum is thought to occur where the amounts of expanded (low density) and collapsed (higher density) structures are equal and thus the most energy is required for their interconversion (using the icosahedral clustering model, this would be where there is 80% ES, as ES necessarily has a collapsed exterior surface). The locus of the specific heat maximum with increasing pressure (called the 'Widom' line) requires the temperature is lowered [1373]. At ambient pressure, the maximum is expected to lie just below the minimum temperature accessible on supercooling (232 K, [215]), although a modeling approach using TIP5P gives ~ 250 K [1352]. The data opposite for supercooled water (upper red line) is taken from [906]. [[◀ Anomalies page : Back to Top ▲](#)]

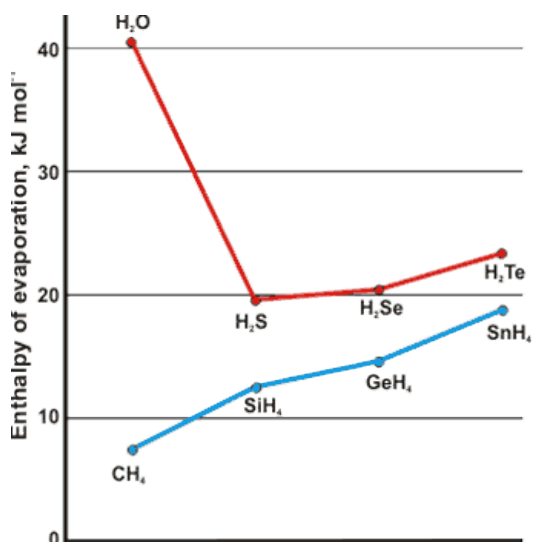
T6 The specific heat capacity (C_p) has a minimum with respect to pressure.

There is a minimum in the heat capacity (C_p) of liquid water with respect to pressure; ~ 400 MPa at 290 K [606]. This may be explained as due to the break-up of the hydrogen bonding as the pressure increases up to about 200 MPa followed by its partial build-up, due to interpenetrating hydrogen bonded networks, at the higher pressures above about 200 MPa. [[◀ Anomalies page : Back to Top ▲](#)]

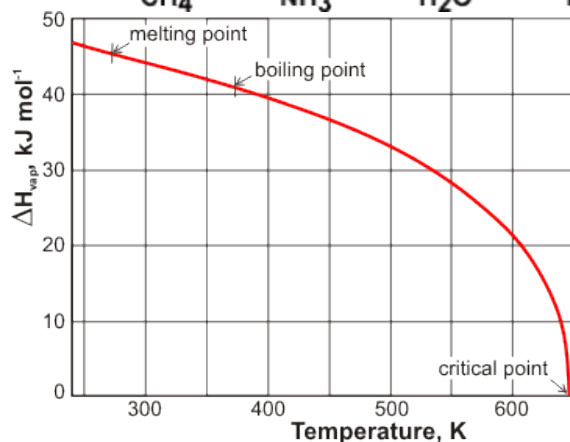
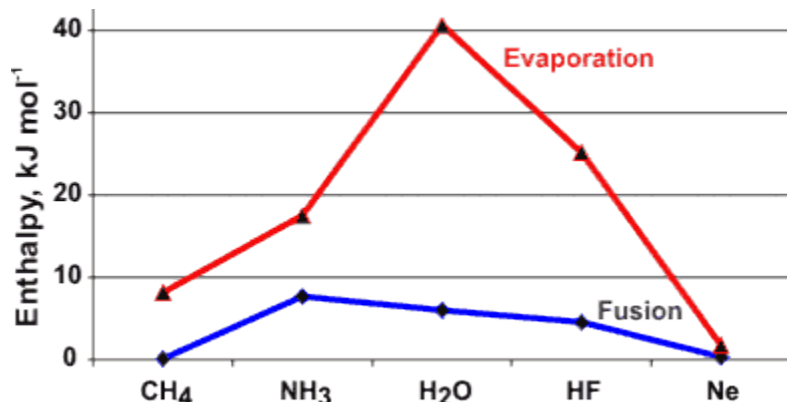
T7 The heat capacity (C_v) has a maximum.

The C_v (the heat capacity at constant volume, $C_v = (\delta U/\delta T)_v$) of liquid water is reported as giving a maximum in the supercooled region (this is not shown in the calculated values graphed above). The increase in C_v in the supercooled region is because most of the anomalous enthalpy change is associated with the anomalous volume change. The decrease in C_v in the more deeply supercooled region is reported as due to the decrease in van der Waals non-bonded dispersion interactions, due to water's low density [682]. [[◀ Anomalies page : Back to Top ▲](#)]

T8 High heat of vaporization (40.7 kJ mol^{-1} , compare $\text{H}_2\text{S } 18.7 \text{ kJ mol}^{-1}$)



Water has the highest heat of vaporization per gram of any molecular liquid (2257 J g^{-1} at boiling point) and hence a high cohesive energy density ($\sim 5 \times \text{CH}_4$, $\sim 4 \times \text{H}_2\text{S}$). There is still considerable hydrogen bonding ($\sim 75\%$) in water at 100°C . As effectively all these bonds need to be broken (very few indeed remaining in the gas phase), there is a great deal of energy required to convert the water to gas, where the water molecules are effectively separated. The increased hydrogen bonding at lower temperatures causes higher heats of vaporization (for example, 44.8 kJ mol^{-1} , at 0°C).



The heat of vaporization reduces to zero at the critical point (see left, [906, 1458]).

The high heat of vaporization also causes water to have an anomalously low ebullioscopic constant (that is, effect of solute on boiling point elevation, 0.51 K kg/mol, compare CCl₄ 4.95 K kg/mol). Also related is the anomalously low cryoscopic constant of water. [[◀ Anomalies page : Back to Top ▲](#)]

T9 High heat of sublimation (51.059 kJ mol⁻¹ at 0 °C).

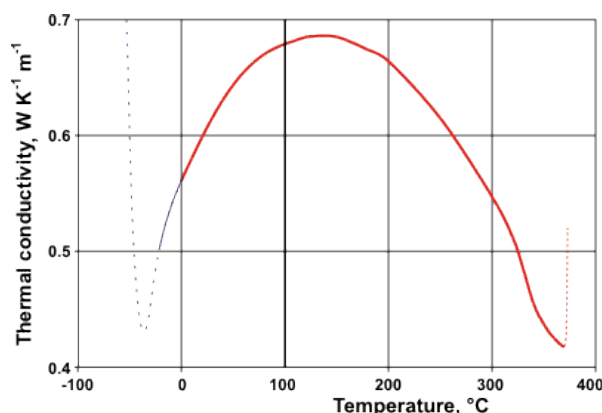
The high heats of fusion and vaporization combine to give rise to an anomalously high heat of sublimation. [[◀ Anomalies page : Back to Top ▲](#)]

T10 High entropy of vaporization (109 J⁻¹ K mol⁻¹, cf. Trouton's constant ~87 J K⁻¹ mol⁻¹).

Water also has anomalously high entropy of vaporization due to the hydrogen-bonded order lost on vaporization in addition to the order lost by virtue of being a liquid changing into a gas. As the heat of vaporization is also anomalously high, the ratio ($\Delta H_{\text{vap}}/\Delta S_{\text{vap}}$) is not anomalous.

Interestingly, the entropy of vaporization is inversely related to the absolute temperature from supercooled water to above 400K (that is, $\Delta S_{\text{vap}} \propto 1/T$). [[◀ Anomalies page : Back to Top ▲](#)]

T11 The thermal conductivity of water is high and rises to a maximum at about 130 °C.



Thermal conductivity along the saturation line (liquid-vapor equilibrium line). Note that the pressure increases with the temperature, see phase diagram. The thermal conductivity becomes infinite at the critical point [IAPWS].

Apart from liquid metals, water has the highest thermal conductivity of any liquid. For most liquids the thermal conductivity (the rate at which energy is transferred down a temperature gradient) falls with increasing temperature but this occurs only above about 130 °C in liquid water [188].

As the temperature of water is lowered, the rate at which energy is transferred is reduced to an ever-increasing extent. Instead of the energy being transferred between molecules, it is stored in the hydrogen bonding fluctuations within the increasingly large clusters that occur at lower temperatures. When the thermal energy is increased it shifts the $ES \rightleftharpoons CS$ equilibrium towards the CS structure, which possesses greater flexibility and has a greater number of bent hydrogen bonds, rather than the transference of kinetic energy. There is a minimum in the thermal conductivity-temperature behavior just below -37 °C as the amount of fully expanded network increases and in line with that indicated by the much higher value found for ice Ih. At lower temperatures, transformation into LDA results in a steeply climbing curve (1.4 W K⁻¹ m⁻¹ at 100 K)

[1202]. Different modeling approaches give a thermal conductivity minimum at ~255 K [1352] or ~230 K [1983].

If the density is kept constant the thermal conductivity is proportional to the square root of the absolute temperature, between 100 °C and 400 °C [614]. [[◀](#) Anomalies page : Back to Top [▲](#)]

Footnotes

^a The full expression is

$$C_p = (\delta H / \delta T)_p = T(\delta S / \delta T)_p = \langle (\Delta S)^2 \rangle_{TP} / k_B = \langle (\Delta H)^2 \rangle_{TPN} / k_B T^2$$

where k_B , P , T , N , V , H and S are the Boltzmann constant, pressure, temperature, number of molecules, volume, enthalpy and entropy respectively; the $\langle \rangle$ brackets indicate the fluctuations in the values about their mean values.

(see [1481]) [Back]

Source:<http://www1.lsbu.ac.uk/water/explan4.html>