

Ice phases

- ◀ Phase diagram
- ◀ Ice crystal data

Water has many solid phases (ices). There are sixteen or so crystalline phases (where the oxygen atoms are in fixed positions relative to each other but the hydrogen atoms may or may not be disordered but obeying the 'ice rules'^j) and three amorphous (non-crystalline) phases. All the crystalline phases of ice involve the water molecules being hydrogen bonded to four neighboring water molecules (see [1300] for a recent review). In most cases the two hydrogen atoms are equivalent, with the water molecules retaining their symmetry, and they all obey the 'ice rules'^j. For the most part, the ordering of the protons (in fixed positions with lower entropy) occurs at lower temperatures, whereas pressure reduces the distances between second shell neighbors (lower volume and greater van der Waals effects). The H-O-H angle in the ice phases is expected to be a little less than the tetrahedral angle (109.47°), at about 107°. The Clausius Clapeyron equationⁿ for many ice phase changes has to be adapted due to water's negative expansion coefficient and anomalous change in entropy with volume [1147c].

| Structural data on the ice polymorphs | | | | | | | | |
|---------------------------------------|--|-------|----------------------|----------------------|--------------|-------------------------------------|---|----------------------------------|
| Ice polymorph | Density, g cm ⁻³ ^a | | Protons ^f | Crystal ^h | Symmetry | Dielectric constant, ϵ_s^i | Notes | |
| Hexagonal ice, I _h | 0.92 | 0.926 | disordered | Hexagonal | $P6_3/mmc$ | one C ₆ | 97.5 | |
| Cubic ice, I _c | 0.93 ^q | 0.933 | disordered | Cubic | $Fd\bar{3}m$ | four C ₃ | | |
| LDA, I _a ^b | 0.925 ^q | | disordered | Non-crystalline | | | As prepared, may be mixtures of several types | |
| HDA ^c | 1.17 | | disordered | Non-crystalline | | | As prepared, may be mixtures of several types | |
| VHDA ^d | 1.25 | | disordered | Non-crystalline | | | | |
| II, Ice-two | 1.17 | 1.195 | ordered | Rhombohedral | $R\bar{3}$ | one C ₃ | 3.66 | |
| III, Ice-three | 1.14 | 1.160 | disordered | Tetragonal | $P4_12_12$ | one C ₄ | 117 | protons may be partially ordered |
| IV, Ice-four | 1.27 | 1.275 | disordered | Rhombohedral | $R\bar{3}c$ | one C ₃ | | metastable in ice V phase space |
| V, Ice-five | 1.23 | 1.233 | disordered | Monoclinic | $C2/c$ | one C ₂ | 144 | protons may be partially |

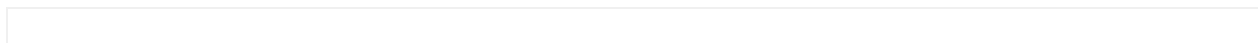
| | | | | | | | | |
|------------------------------|-------|-----------|------------------------------------|---------------------------|--------------|-------------|------|---|
| | | | | | | | | ordered |
| VI, Ice-six | 1.31 | 1.31 4 | disordered | Tetragonal ^e | $P4_2/nmc$ | one C_4 | 193 | two interpenetrating frameworks |
| VII, Ice-seven | 1.50 | 1.59 1 | disordered | Cubic ^e | $Pn\bar{3}m$ | four C_3 | 150 | two interpenetrating ice Ic frameworks |
| VIII, Ice-eight | 1.46 | 1.88 5 | ordered | Tetragonal ^e | $I4_1/amd$ | one C_4 | 4 | low temperature form of ice VII |
| IX, Ice-nine | 1.16 | 1.16 0 | ordered | Tetragonal | $P4_12_12$ | one C_4 | 3.74 | low temperature form of ice III, metastable in ice II space |
| X, Ice-ten | 2.51 | 2.78 5 | symmetric | Cubic ^e | $Pn\bar{3}m$ | four C_3 | | symmetric proton form of ice VII |
| XI, Ice-eleven | 0.92 | 0.93 0 | ordered | Orthorhombic | $Cmc2_1$ | three C_2 | | low temperature form of ice Ih |
| XI, Ice-eleven ^k | >2.51 | | symmetric | Orthorhombic ^e | $PBcm$ | distorted | | Superionic |
| Metallic [1818] ^k | | ~12° | symmetric C_2 , O-H-O bent | Monoclinic ^e | $C2/m$ | | | Superionic |
| XII, Ice-twelve | 1.29 | 1.30 1 | disordered | Tetragonal | $I\bar{4}2d$ | one C_4 | | metastable in ice V phase space |
| XIII, Ice-thirteen | 1.23 | 1.24 7 | ordered | Monoclinic | $P2_1/a$ | one C_2 | | ordered form of ice V phase |
| XIV, Ice-fourteen | 1.29 | 1.29 4 | mostly ordered | Orthorhombic | $P2_12_12_1$ | one C_4 | | ordered form of ice XII phase |
| XV, Ice-fifteen | 1.30 | 1.32 8 | ordered | Pseudo-orthorhombic | $P\bar{1}$ | one C_4 | | ordered form of ice VI phase |

Two different forms of ice-eleven have been described by different research groups: (a) the high-pressure form (also known as ice-thirteen) involves hydrogen atoms equally-spaced between the oxygen atoms [84] (like ice-ten) in a distorted hexagonal close packed structure whereas (b) the lower pressure, low temperature, form uses the incorporation of hydroxide defect doping (and interstitial K⁺ ions) to order the hydrogen bonding of ice Ih [207], that otherwise occurs too slowly. Another ice-ten has been described, being the proton ordered form of ice-six (VI); this is now known as ice fifteen. Only hexagonal ice-one (Ih), ice-three (III), ice-five (V), ice-six (VI), ice-seven (VII) and, perhaps, ice-ten (X) can be in equilibrium with liquid water (ice-ten with

supercritical water), whereas all the others ices, including ice-two (II, [273]), are not stable in its presence under any conditions of temperature and pressure. The low-temperature ices, ice-two, ice-eight(VIII), ice-nine (IX), ice-eleven (low pressure form), ice-thirteen (XIII) [1002], ice-fourteen (XIV) [1002] and ice fifteen(XV) [1582] all possess (ice-nine and ice-fourteen incompletely) low entropy ordered hydrogen-bonding whereas in the other ices (except ice-ten [80] and ice-eleven where the hydrogen atoms are symmetrically placed and molecules of H₂O do not have individual existence) the hydrogen-bonding is disordered even down to 0 K, where reachable. Ice-four (IV) and ice-twelve (XII) [82] are both metastable within the ice-five phase space. Cubic ice (Ic) is metastable with respect to hexagonal ice (Ih). It is worth emphasizing that liquid water is stable throughout its phase space above. However, ice-seven(VII) undergoes X-ray-induced (~9.7 keV) dissociation to an O₂ - H₂ alloy at high pressure (>2.5 GPa) but reverts to ice-seven near its melting point at 700 K and 15 GPa [1383]. A new ice phase has been reported to lie on what had been thought to be the liquid (supercritical) side of ice-seven at high pressures, with approximate triple points of about 700 K, 20 GPa with liquid (supercritical) water and ice-seven and about 1500 K, 40 GPa with liquid (supercritical) and ice-ten [1521]. This may be a plastic phase where only molecular rotations are allowed [2078]. However, the state of water in this part of the phase diagram is confused. Others propose a new superionic phase here with an approximate triple point of about 1000 K, 40 GPa with liquid (supercritical and ionized) water and ice-seven at high temperatures (~1500K) [1572], a partially ionic phase consisting of alternate layers of OH⁻ and H₃O⁺ at low temperatures [1810] or several new phases converting into one where the coordination number of oxygen increases from 4 to 5 with a significant increase of density [1818].




Kurt Vonnegut's highly entertaining story concerning an (imaginary) ice-nine, which was capable of crystallizing all the water in the world [83], fortunately has no scientific basis (see also I_E). Ice-nine, in reality, is a proton ordered form of ice-three, and only exists at very low temperatures and high pressures and cannot exist alongside liquid water under any conditions. Ice Ih may be metastable with respect to empty clathrate structures of lower density under negative pressure conditions (that is, stretched) at very low temperatures [520].



| More structural data on the ice polymorphs | | | | | |
|--|------------------------|---|--------|---|----------------------------|
| Ice polymorph | Molecular environments | Small ring size(s) ^p | Helix | Approximate O-O-O angles, ° | Ring penetration hole size |
| Hexagonal ice, Ih | 1 | 6 | None | All 109.47±0.16 | None |
| Cubic ice, Ic | 1 | 6 | None | 109.47 | None |
| LDA, Ia ^b | 3+ | 5(9), 6(55) | None | mainly 108, 109 and 111 | None |
| HDA ^c | 6+ | 5(9), 6(55) | None | broad range | None |
| VHDA ^d | 6+ | 5(9), 6(55) | None | broad range | None [747] |
| II, Ice-two | 2 (1:1) | 6(7), 8(9),10(15) | None | 80,100,107,118,124,128; 86,87,114,116,128,130 | None |
| III, Ice-three | 2 (1:2) | 5(1), 7(1), 8(1) | 4—fold | (1) 91,95,112,112,125,125 (2) 98,98,102,106,114,135 | None |
| IV, Ice-four | 2 (1:3) | 6(7), 8(18),10(42) | None | (1) 92,92,92,124,124,124 (3) 88,90,113,119,123,128 | some 6 |
| V, Ice-five | 4 (1:2:2:2) | 4(2), 5(3), 6(2), 8(3),9(2),10(12),12(1) | None | (1) 82,82,102,131,131,131 (2) 88,91,109,114,118,128 (3) 85,91,101,103,130,135 (4) 84,93,95,123,125,126 | 8 (1 bond) |
| VI, Ice-six | 2 (1:4) | 4(5), 8(9) | None | (1) 77,77,128,128,128,128 (2) 78,89,89,128,128,128 | 8 (2 bond) |
| VII, Ice-seven | 1 | 6 | None | 109.47 | every 6 |
| VIII, Ice-eight | 1 | 6 | None | 109.47 | every 6 |
| IX, Ice-nine | 2 (1:2) | 5(1), 7(1), 8(1) | 4—fold | (1) 91,95,112,112,125,125 (2) 98,98,102,106,114,135 | None |
| X, Ice-ten | 1 | 6 | None | 109.47 | every 6 |
| XI, Ice-eleven | 1 | 6 | None | 109.47 | None |
| XI, Ice-eleven ^k | undetermined | 6/4 | None | undetermined | every 6 |
| XII, Ice-twelve | 2 (1:2) | 7(2), 8(3) | 5—fold | (1) 107,107,107,107,115,115 (2) 67,83,93,106,117,132 | None |
| XIII, Ice-thirteen | 7 (all equal) | 4(2), 5(3), 6(2), 8(3),9(2),10(12),12(1) | None | (1) 82,82,102,131,131,131 (2) 88,91,109,114,118,128 (3) 85,91,101,103,130,135 (4) 84,93,95,123,125,126 | 8 (1 bond) |
| XIV, Ice-fourteen | 2 (1:2) | 7(2), 8(3) | 5—fold | (1) 107,107,107,107,115,115 (2) 67,83,93,106,117,132 | None |
| XV, Ice-fifteen | 2 (1:4) | 4(5), 8(9) | None | (1) 77,77,122,122,134,134 (2) 87,90,94,124,129,135 | 8 (2 bond) |

The thermal conductivities properties of crystalline and amorphous ices have been reviewed [1202]. Other stable or metastable phases of ice have been proposed (for example, Ice XIII and ice XIV were proposed earlier than their discovery [958]) but their structures were not established. Several new phases (for example ice i, 'Hexagonal Bilayer Water' and 'Pleated Sheet Water', [1985]) have only been found (so far) in modeling studies, but other ices have been found at confined surfaces. 'Metallic' water, where electrons are freed to move extensively throughout the material and the atoms of water exist as ions, probably exists as an antiferrotype structure^m above 1.76 TPa [1138]. It is not thought that any other phases are stable at higher pressures than this.

The proposed topology of the transformations between ice XI \longrightarrow ice II \longrightarrow ice IX and ice VIII \longrightarrow ice X has been described [1237]. [[Back to Top](#) 

Footnotes

^a Left column: experimental density at atmospheric pressure but temperature of stability (this will contain crystal boundaries and faults); right column: crystallographic density [1717]. [[Back](#)]

^b Low-density amorphous ice (LDA). The structural data in the Table is given assuming LDA has the structure of ES. [[Back](#)]

^c High-density amorphous ice (HDA). The structural data in the Table is given assuming HDA has the structure of crushedCS. [[Back](#)]

^d Very high-density amorphous ice (VHDA). The structural data in the Table assumes no hydrogen bond rearrangements from LDA or HDA. As VHDA is likely to be a relaxed form of HDA, this assumption seems unlikely [935]. [[Back](#)]

^e Structure consists of two interpenetrating frameworks. [[Back](#)]

^f Although primarily ordered or disordered, ordered arrangements of hydrogen bonding may not be perfect and disordered arrangements of hydrogen bonding are not totally random as there are correlated and non-bonded preferential effects. [[Back](#)]

^g This ice is reported to be more likely a trigonal structure made up of $2\text{H}_3\text{O}^{\delta+} + \text{O}_2^{\delta-} + \text{H}_2$ rather than a $2\text{H}_2 + \text{O}_2$ alloy [1419]. [[Back](#)]

^h Crystal cell parameters have been collated. The right-hand column gives the space group. [[Back](#)]

ⁱ Dielectric constants fall into two categories dependent on whether the hydrogen bonds are ordered (low values) or disordered (high values). [[Back](#)]

^j **The 'ice rules'**: each water molecule has four hydrogen-bonded neighbors, two hydrogen atoms near each oxygen ($\sim 1 \text{ \AA}$), one hydrogen atom on each $\text{O}\cdots\text{O}$ bond; thus $\text{H-O-H}\cdots\text{OH}_2$ and $\text{H}_2\text{O}\cdots\text{H-O-H}$ are allowed but $\text{H-O-H}\cdots\text{H-O-H}$ and $\text{H}_2\text{O}\cdots\text{OH}_2$ are not). In hexagonal ice this disorder gives rise to a zero-point entropy of $3.41 \text{ J mol}^{-1} \text{ K}^{-1}$. This is close to $R \cdot \ln(3/2) = 3.371 \text{ J mol}^{-1} \text{ K}^{-1}$, which makes no allowance for correlations introduced by closed hydrogen-bonded loops; see [717] for a discussion of this point. A recent estimate of the zero-point entropy is $R \cdot \ln(1.507606) = 3.4133 \text{ J mol}^{-1} \text{ K}^{-1}$ [1090]. As the H-O-H angles are about 106.6° [717], the hydrogen bonds are not straight

(although shown so in the figures). Weaknesses (Bjerrum defects) in the ice crystal are apparent where the ice rules are disobeyed. Both O····O contacts, without an intervening proton (L defect) and O-H····H-O contacts (D defect, with two protons between the pair of oxygen atoms) may occur due to molecular rotations where neighboring water molecules fail to adjust their hydrogen bonding. Other defects may be caused by the presence of H₃O⁺ and OH⁻ ions. [Back]

^k Ice XI is also known as ice XIII. These structures have not been experimentally verified and, therefore perhaps, are best not referred to with the numerical designations first used. Density functional calculations [1709] indicate a pressure-induced initial displacement of the ice-ten atomic layers to give an orthorhombic *Pbcm* structure. At higher pressure, this may be followed by the squeezing of the H-atoms from their midpoints to give a *Pbca* structure and then, at over a terapascal, to a metallic ice, consisting of corrugated sheets of H and O atoms with the H-atoms at the octahedral midpoints between next-nearest oxygen atoms [1709]. An alternative view is that the orthorhombic *Pbcm* structure is superseded by a *Pmc2₁* phase above 930 GPa, followed by a *P2₁* crystal structure at about 1.3 TPa and finally the metallic *C2/m* phase above about 4.8 TPa [1818]. Such ice is not molecular and consists of protons and oxygen dianions with mobile electrons [1666] and is expected at the core of giant planets such as Jupiter and Saturn. [Back]

^m The antifluorite structure consists of an face centered cubic (FCC) unit cell with oxygen anions occupying the FCC lattice points (corners and faces) and hydrogen cations occupy the eight tetrahedral sites within the FCC lattice. [Back]

ⁿ The Clausius Clapeyron equation can be stated as $dT/dP = T\Delta V/\Delta H = \Delta V/\Delta S$ where P, T, H, V and S are the pressure, temperature, enthalpy, volume and entropy. This may be extended to be $dT/dP = T(\text{sign } \alpha_2 V_2 - \text{sign } \alpha_1 V_1)\Delta V/\Delta H$, where α represents the thermal expansion coefficients, for use with phases with negative expansion coefficients including the ice phase changes LDA → Ic, HDA → LDA, LDA → HDA, III → V, V → VI, VI → VII and VI → VIII [1147b]. [Back]

^o At 5 TPa. [Back]

^p The figures in brackets are the relative number of such rings. For the crystalline ices they are from [2021].

^q Data corrected to 0 °C, for direct comparison to ice 1h. The densities were determined at ~ 80 K (ice 1h 0.932 g.cm⁻³, ice 1c 0.943 g.cm⁻³, LDA 0.937 g.cm⁻³) [2032]. [Back]

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